

***Report on Best Available Techniques (BAT)***  
***in***  
***German Zinc and Lead Production***

**FINAL DRAFT**

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## Glossary

AOX	Adsorbable Organic Halogen Compounds	IS/ISP	Imperial smelting/Imperial smelting process
BAT	Best Available Techniques	KHD	German Engineering Company
BImSchV	BundesImmissionsschutzverordnung	LAI	Länderausschuß Immissionsschutz
BSB	Blei- und Silberhütte Braubach (German secondary lead plant)	L1-L10	Lead producing company/plant number 1-10
BSN	Badische Stahl-Nebenprodukte GmbH	M.I.M.	Mount Isa Mining
DEVS4	Leaching test according to German DIN 38 414	n. a.	not available
DIN	Deutsches Institut für Normung	PE/ PP	Polyethylene/ Polypropylene
EAF	Electric arc furnace	QSL	Queneau-Schuhmann-Lurgi
EFÜ	Emissionsdatenfern-Überwachung	SHG	Special High Grade
EN	European Norm	SLI	Starting, Lighting, Ignition
ESP	Electrostatic precipitator	TA	Technical Instructions
EU	European Union	TBRC	Top Blown Rotary Converter
GOB	Good Ordinary Brand	TE	Toxic Equivalent
HMIP	Her Majesty's Inspectorate of pollution (UK)	TVo	Limit value for eluate according to German regulations (drinking water)
IPPC	Integrated Pollution Prevention and Control (IPPC-Directive)	Z1-Z8	Zinc producing company/plant number 1-8

## Chemical Symbols

Ag	Silver	F	Fluorine	NO <sub>x</sub>	Nitrogen oxide
Al <sub>2</sub> O <sub>3</sub>	Aluminium oxide	Fe	Iron	Pb	Lead
As	Arsenic	FeO	Iron oxide	PbO	Lead oxide
C	Carbon	H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid	PCDD/PCDF	Dioxins/furans
Ca	Calcium	HCl	Hydrogene chlorine	S	Sulphur
CaO	Calcium oxide, lime	K <sub>2</sub> O	Potassium oxide	Sb	Antimony
Cd	Cadmium	MgO	Magnesium oxide, magnesia	SiO <sub>2</sub>	Silica, silicon oxide
Cl <sub>2</sub>	Chlorine	MnO	Manganous oxide	SO <sub>2</sub>	Sulphur dioxide
Cr <sub>tot</sub>	Chromium (total)	Ni	Nickel	Zn	Zinc
Cu	Copper	NO <sub>2</sub>	Nitrogene dioxide	ZnO	Zinc oxide

## Units

µg	Microgramme	kg	Kilogramme	Nm <sup>3</sup>	Norm cubic metre (STP)
a	Year	kWh	Kilowatt hour	ng	Nanogramme
cm	Centi metre	l	Litre	ppm	Parts per million
d	Day	m <sup>3</sup>	metre, Cubic metre	rpm	Rotations per minute
DM	Deutsche Mark	mg	Milligramme	t	Ton
g	Gramme	mm	Milli metre	wt.-%	Weight-percent
GJ	Gigajoule	Mio.	Million	°C	Degrees Celsius
h	Hour	MWh	Megawatt hour		

## Preface

On September, 24th, 1996 the Council of the European Communities issued the Directive 96/61/EC on Integrated Pollution Prevention and Control (IPPC-D). This directive aims to achieve a high level of protection of the environment taken as a whole. It was enacted especially considering the common environmental goals of the EC, laid down in article 130r, EC-treaty (conservation and protection of the environment and improvement of environmental quality (i), protection of human health (ii), sustainable use of resources (iii), promotion of measures on an international level to handle regional or global environmental problems (iv)), and being aware of the fact that the implementation of an integrated concept of pollution prevention needs to be addressed by measures on a community level.

Annex I of directive 96/61/EC contains an extensive list of industrial activities to which the directive applies. According to this list, also industrial activities related to the production and processing of metals are subject to the measures within the IPPC (Nr.2). The directive provides a general framework with principles for integrated pollution prevention and control. The goal of this integrated concept is to protect the environment taken as a whole by preventing and controlling emissions into all environmental media. The necessity for drawing up information on best available techniques (BAT) for certain industrial activities is constituted by some of the measures laid down within the directive to attain the above mentioned goal:

- the definition of basic obligations, that operators of industrial activities have to comply with (art 3, esp. 3 a)).
- the requirement for the EC-member states to ensure compliance with these basic obligations by the operators (art 3, 4, 5).
- the definition of an approval procedure according to which permits shall be granted, only if operators fulfil a number of requirements, further specified in the directive (art 3, 6, 7, 8).
- the reminder to the competent authorities, that a permit has to include emission limit values for at least a minimum number of substances explicitly named in Annex III. These emission limit values, or possibly equivalent parameters or technical measures, shall be based on reference values derived from so-called BAT (BAT, art 9(3)). The IPPC specifies explicitly, that BAT themselves are not binding, but only derived reference values.
- the specification of the term BAT in the IPPC as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole" (art 2.11).
- the obligation for the member states to provide the EC-Commission with representative data and possibly information about BAT for the categories of industrial activities listed in Annex

I (art 16.1). Furthermore the EC-Commission is urged to maintain an information exchange between the member states and the concerned industries about BAT, related control measures, and developments in these fields (art 16.2). Additionally the member states have to ensure that the competent authorities follow or are informed of developments in BAT (art 11).

In particular the articles dealing with the definition of BAT and requiring an exchange of information on BAT are the motive for this document (esp. art 16.2). The goal of this study is to provide background information on BAT for environmental protection within the German zinc and lead production industry that serve as possible candidates BAT on an EU level. It gives information on environmental protection techniques but also production techniques on this performance. Further processing steps are not included in this study. The paper is based also on literature study, but mainly on technical discussions with the members of the different national working groups: *Zinc-BAT*, *Lead-BAT* and "BVT-Abstimmungsgruppe".

The document is structured as follows:

Chapter 1 provides general information about the zinc and lead industry, including first indications of environmental concerns regarding the production of zinc and lead. Then basic information about the applied processes and techniques in the zinc and lead and the main outputs and their sources are investigated (Chapter 2). In Chapter 3, German zinc and lead production plants are described, including input/output levels and emission levels. Chapter 4 contains a list of German candidates BAT for being possibly BAT on an EU level. A collection of so-called emerging techniques is presented in Chapter 5. Finally, an overview of relevant national and international legislation is provided in the Annex (Chapter 7).

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## 1 General information

### 1.1 Production and use of zinc and lead

Germany is one of the main producers and users of non-ferrous metals in the European Community. Other important producers and consumers are France, Belgium, Italy, Spain, the Netherlands and the United Kingdom. In the following, information on production, use and recycling is given for the individual branches zinc and lead. The production of copper is covered by a separate report. The production of aluminium, other light metals or heavy metals is not in the scope of this study.

#### 1.1.1 Zinc

Zinc is one of the major non-ferrous metals used in modern industry. It is the fourth metal in terms of consumption, ranking behind iron, aluminium and copper [34]. Zinc is traded in various qualities and shapes: metal ingots of different grades, extrusion products (bars, rods and wires), rolling products (sheets, strips), casting alloys, powders and chemical compounds (zinc oxides). It is essential for a lot of high-tech products in industrial production.<sup>1</sup> The main *first-use* of zinc world-wide is the protection of iron and steel from corrosion with a share of about 47 % of the total zinc produced. Besides galvanising for steel protection, the other main uses for zinc are in the brass industry (19 %), zinc base alloys (14 %), zinc semi-finished products (8 %), chemicals (8 %), zinc dust/powder (1 %) and others. *End-uses* for zinc world-wide are the building and construction industry (48 %), transport (23 %), consumer durables, batteries and others (10 %), and industrial as well as commercial machinery and equipment (10 %) [34]. In Germany (1996), the first-uses are galvanising (32 %), brass industry (26 %), die casting (6 %), zinc semi-finished products (26 %) and others (10%).

Today, about 30 % of the total zinc consumed world-wide comes from secondary raw materials. The main sources of zinc for recycling are [34]:

- old/new brass scrap (32 %),
- galvanising residues (23 %),
- old/new die casting scrap (16 %),
- old/new zinc sheet (10 %),
- flue dust from steel plants (8 %), and
- others, like chemical industry residues or old slag from smelters (11 %).

---

<sup>1</sup> Detailed information on physical and chemical properties as well as the industrial uses of zinc can be found elsewhere (c.f. [29], [34], [66], [59]).

**Table 1-1: Zinc production and use in Germany, the EU and world-wide**

Year	Germany <sup>*)</sup> [Mio. t]		EU <sup>*)</sup> [Mio. t]		World-wide <sup>*)</sup> [Mio. t]	
	Refined zinc production	Use	Refined zinc production	Use	Refined zinc Production	Use
1983	0.356	0.409	1.299	1.301	6.384	6.370
1985	0.367	0.409	1.373	1.312	6.870	6.532
1987	0.380	0.455	1.667	1.491	7.035	6.959
1988	0.356	0.450	1.708	1.570	6.856	6.848
1989	0.354	0.453	1.686	1.585	6.787	6.714
1990	0.338	0.484	1.699	1.655	6.691	6.666
1991	0.346	0.540	1.765	1.738	6.854	6.627
1992	0.383	0.532	1.827	1.711	6.953	6.557
1993	0.381	0.492	1.811	1.640	7.184	6.608
1994	0.360	0.519	1.922	1.892	7.131	6.981
1995	0.322	0.505	1.960	2.007	7.327	7.489
1996	0.328	0.480	1.980	1.929	7.428	7.533
1997	0.318	0.486	1.968	1.966	7.736	7.720

<sup>\*)</sup> The production of remelted zinc and zinc dust is excluded.

Source: Bundesamt für Wirtschaft [11], Rentz et al. [72], International Zinc Association [34], Graf [29], others

Zinc is traded in different qualities. Moreover, during the course of zinc production several raw materials are processed and different intermediate products arise. For reasons of clarification, Table 1-2 gives a short description of the main zinc and zinc alloy qualities, by-products and intermediate products.

**Table 1-2: Glossary: Main zinc products**

Name	Characteristics	Main uses
Zinc blende	Sphalerite, ZnS	Most important zinc mineral today
Calcine	Roasted zinc concentrates	Intermediate product (roasted zinc blende)
Raw or crude zinc	Impure (pyrometallurgical) zinc	Intermediate product for further refining
Zinc, SHG	Special high grade, highest quality 99.995 % pure (hydro-, or pyrometallurgical refined)	Standard sale product
Zinc, GOB	Good ordinary brand, more than 98.5 % pure	Sale product
Zinc alloys (e.g. ZL 0410, ZL 0430)	According to DIN/EN	Die casting (automotive)
Secondary zinc	According to DIN/EN	Galvanising
Brass, different qualities	Copper-zinc alloys	Several applications in the brass industry
Zinc dross	Metals/metal oxides mixture	By-product, recycling
Hard zinc	Impure zinc	Zinc oxide production

### 1.1.2 Lead

Lead is one of the major non-ferrous metals used in modern industry. Table 1-3 shows lead production and use in Germany, the EU and world-wide. In the European Union the main lead producing countries are the United Kingdom, Germany, France, Belgium, and Italy and with a minor share Spain and Sweden. The main lead using countries are Germany, the United Kingdom, France, Italy and Spain.

The main industrial users are the producers of lead-acid batteries with a share of about 60 - 70 % (about 3.3 - 3.8 million tons). World-wide 300 - 350 million of lead batteries are manufactured per year, and the demand for the battery industry is growing; the estimations for the future share differ between 75 and 80 % [7]. Though with a growing market for electric cars the research for new, alternative battery systems, like nickel-cadmium or nickel-metal hydride, will be intensified [92]. Other users of lead and lead compounds are the medical equipment manufactures and nuclear industry, the printing industry and the construction industry. The main uses are for the protection from corrosion and from ionising radiation, sound insulation and the production of special glasses. The gasoline additive market ("antiknock") has nearly disappeared.

**Table 1-3: Lead production and use in Germany, EU and world-wide**

Year	Germany [Mio. t]		EU [Mio. t]		World-wide [Mio. t]	
	Refined lead production	Use	Refined lead production	Use	Refined lead Production	Use
1983	0.353	0.318	1.175	1.200	4.991	4.958
1985	0.356	0.345	1.214	1.219	5.317	5.169
1987	0.340	0.345	1.374	1.378	5.411	5.334
1988	0.345	0.374	1.441	1.423	5.518	5.420
1989	0.350	0.375	1.422	1.478	5.690	5.600
1990	0.349	0.392	1.389	1.513	5.419	5.407
1991	0.363	0.414	1.425	1.503	5.299	5.216
1992	0.354	0.412	1.372	1.454	5.314	5.168
1993	0.334	0.350	1.356	1.348	5.429	5.146
1994	0.332	0.354	1.569	1.604	5.464	5.493
1995	0.314	0.360	1.541	1.685	5.762	5.866
1996	0.238	0.342	1.520	1.659	5.881	6.033
1997	0.329	0.336	1.613	1.647	5.975	5.977

Source: Bundesamt für Wirtschaft [11], Rentz et al. [72], International Lead and Zinc Study Group [33]

The main lead users in Germany are shown in Table 1-4 (1996).

**Table 1-4: Main lead users in Germany (1996)**

Usage	[t/a]	[%]
Lead-acid batteries	192,772	58.2
Chemical products	68,932	20.8
Intermediate products	46,596	14.1
Cable sheaths	7,916	2.4
Alloys	7,549	2.3
Shape cast	6,466	1.9
Diverse	787	0.2
In total	331,018	100

Source: according to VARTA Recycling GmbH [91]

Future trends in lead use are related to the growth of economics. On the other hand, concerns about the toxicity of lead and lead compounds could still prevent or limit the usage of lead in several applications.

Lead is recycled to a high percentage; only about half of the total lead production originates from primary lead smelters. However, world-wide more than 85 % of primary lead is still produced with the conventional updraft and to a small extent with the old-styled downdraft Dwight-Lloyd sinter machines and blast furnace operation (sinter plant - blast furnace route). World-wide, 220 plants and units in 53 countries are involved in secondary lead production. The annual output capacity of lead bullion from these plants ranges between below 5,000 t (about 80 plants) and above 50,000 t (about 18 plants) [61]. So the scale of plants is often smaller in the secondary sector compared to the primary plants. In Germany, the share of secondary lead production is substantially higher compared to most other countries due to the fact that the recycling activities in the lead-acid battery sector are very successful and reach rates of over 95 % [115]. According to [92], in Germany 54 % of the total lead processed comes from recycled materials (1996). Every year in Germany, more than 10 million lead-acid batteries are collected for recycling. Detailed information about the organisation and the strategies in the lead-acid battery recycling sector can be found elsewhere ([7], [115], [116]).

Lead is traded in different qualities. Moreover, during the course of lead production several intermediate and by-products arise. For clarification purposes, the glossary in Table 1-5 gives a description of the main lead qualities, as well as the intermediate products and by-products from lead production.<sup>2</sup>

---

<sup>2</sup> Detailed information on physical and chemical properties of lead can be found elsewhere (c.f. [83], [66]).

**Table 1-5: Glossary: lead and lead alloy qualities, intermediate products and by-products**

	Name	Characteristics	Main uses
<b>Lead</b>	Refined lead (commercially pure lead/high purity lead)	99.9 % - 99.99 % lead normally cast into ingots	Battery manufacturing, other industrial uses
<b>Lead alloys</b>	Calcium lead	Lead-calcium (tin) alloy	Manufacturing of low-maintenance batteries
	Antimony (or hard) lead	Lead alloyed with antimony and arsenic	Battery manufacturing
	Corroding lead	Lead alloyed with copper	Cable production
<b>Intermediate products</b>	Lead bullion	Lead with 90 - 98 % purity	Refining
	Matte	Sulphidic product from smelting (containing Fe, Pb, Cu, S)	Selling to copper plants for copper recovery
	Speiss	Fraction containing Fe, Cu, Ni, As, Sb and precious metals	Sold to special refiners
	Dross	Fraction with different compositions depending on purification step	Internal or external treatment
	Flue dusts	Dust containing mainly lead, chloride, cadmium	Internal or external treatment
<b>By-products</b>	Slag	Iron-calcium silicates	Road construction

## 1.2 First indication of environmental concerns regarding the production of zinc and lead

Plants producing non-ferrous metals such as zinc and lead are a source for certain emissions into the atmosphere and for discharges into water as well as for solid residues. A short description of relevant pollutants will be given in the following sections as a first indication. Emissions causing odours or noise have to be taken into account according to the IPPC-Directive. However these emissions have to be looked at on a plant by plant basis. Therefore they are not covered by the following general section.

### 1.2.1 Emissions into the atmosphere

The processing of non-ferrous metals is a source of different kinds of air polluting substances above all for particulate matter and gases. Depending on their origin two kinds of atmospheric emissions can be distinguished: Emissions arising e.g. from furnaces, which can usually be captured, cleaned by appropriate gas cleaning devices and released via a stack (controlled or stack emissions). Fugitive emissions are mainly caused by open handling and storing of materials. Other sources are roofs and openings of production buildings as well as inadequately enclosed transport systems and leakages. Fugitive emissions should be avoided by hoods, closed transport systems and good housekeeping.

Osparcom [65] defines the following atmospheric contaminants to be taken into consideration for the (primary) production of non-ferrous metals:

- particulate matter,
- antimony, arsenic, cadmium, cobalt, copper, lead, mercury, nickel, selenium, tin, zinc, and
- chlorine, fluorine, nitrogen oxides, sulphur, sulphur dioxide and sulphuric acid mists.

*Particulate matter* is produced during all smelting operations used in the non-ferrous metal industry. The flue dusts contain various metals and are treated internally or externally to recover the metal content. *Sulphur dioxide* emissions arise due to the processing of sulphur containing raw materials and fuels in the different production routes. According to the German Umweltbundesamt<sup>3</sup> (c.f. [87], [88]), the estimated emissions of sulphur dioxide in the German non-ferrous metal industry amounted to about 4,400 t/a in 1994, which accounts for 5.2 % of the sulphur dioxide emissions from the industrial processes<sup>4</sup> and for 0.15 % of the overall sulphur dioxide emissions in Germany. The estimated emissions of nitrogen oxides<sup>5</sup> amounted to about 1,200 t/a in 1994, which accounts for 5.1 % of the nitrogen oxide emissions from the industrial processes and for 0.05 % of the overall nitrogen oxide emissions in Germany. Non-ferrous metal plants are a source of *heavy metal emissions*. On one hand heavy metals are highly concentrated in the processed raw materials and products, on the other hand the high temperatures in the production processes lead to the volatilisation of heavy metals and their compounds. Due to the large number of different raw materials used and the various processes applied, nearly all kinds of heavy metals and heavy metal compounds may be emitted [114]. Jockel calculates a rough estimation of the controlled overall annual heavy metal emissions and emission factors from German non-ferrous metal production plants for different years (1985, 1990, 1995) partly based on individual measurements in the 80's (c.f. [35]). These values do not present the current state of technology applied in German production plants and cannot be considered as representative. Therefore these values may deviate considerably from the figures stated in Chapter 3 in the study on hand.

*Dioxins and furans (PCDD/PCDF)* have been seen as a further problem in the non-ferrous metal industry. Their formation depends for instance on the type of raw materials and fuel used as well as on the technical process chosen. Different measures are available to control the PCDD/PCDF emissions from the non-ferrous metal production plants.

---

<sup>3</sup> This calculation is based on estimated emission factors for sulphur dioxide (nitrogen oxides) which results from the processing of raw materials and the usage of different energy sources. The validity of this emissions factors should be checked.

<sup>4</sup> Emissions caused by energy generation processes are not included in the figure for the industrial processes.

<sup>5</sup> NO<sub>x</sub> given as NO<sub>2</sub>.

### 1.2.2 Potential releases into water

In the non-ferrous metal industry, water is used for different purposes mainly dependent on process specific constraints (see also [65]). Controlled discharges, such as process effluent or cooling water take place through well defined ducts. They are usually treated in a waste water treatment plant before being released. In order to prevent uncontrolled discharges, that may arise due to leakages or accidents, measures such as collecting basins are applied. In general, surface run-off from the plant site is captured and treated either in a waste water treatment plant or in a special run-off water treatment plant. In non-ferrous metal plants, effluents may arise at different sources [23], mainly:

- wet gas cleaning
- slag granulation
- hydrometallurgical treatment (of oxidic materials),
- electrolytic processes,
- cooling water, and
- surface run-off.

Osparcom [65] gives a list of potential contaminants into water and soil which could arise in the production processes of the (primary) non-ferrous metal industry:

- suspended solids,
- arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, thallium, tin, tungsten, zinc, and
- sulphate and sulphite.

In addition, the pH-value should be taken into account. Cooling water for indirect cooling from an open cooling circuit or a once-through system is not contaminated and therefore does not have to be cleaned. Cooling water for slag granulation is led through a closed circuit without conditioning agent and normally does not have to undergo demineralisation. Effluents from the demineralisation of closed cooling circuits are treated in a waste water treatment plant.

### 1.2.3 Solid materials generated

Besides the main products, solid materials generated in the non-ferrous metal industry are slags, precipitates, residues from the production, dusts and sludges from flue gas control, and sludges from the waste water treatment. Residues for recovery are recycled in a production process, either in the same plant or in an external plant at a different location. In general, only a few residues arise in non-ferrous metal plants as the traditional aim of the process techniques is to close production loops to recover the metals contained and to generate marketable by-products. In the zinc and lead industries only a minor amount of non-usable residues has to be disposed off.





## **2 Applied process technology and abatement techniques in German zinc and lead production**

Due to the large number of activities in the production of zinc and lead and the existing site specific differences, in this technical study only brief descriptions of the applied process technology and abatement techniques are given.

### **2.1 Introduction and scope of the study**

Integrated pollution prevention and control require the consideration and prevention and/or minimisation of all harmful impacts on the environment caused by industrial activities at the same time. Also the shifting of pollution from one environmental media to another has to be taken into account.

The goal of the IPPC-Directive (IPPC-D) is to prevent or control pollution caused by certain industrial activities, including the primary and secondary production of non-ferrous metals (c.f. Art 1 and Annex I). As mentioned in the preface of this paper, it therefore requires the member states of the EU, inter alia, to exchange information about BAT for these activities. Within the IPPC-D pollution is defined to be "the direct or indirect introduction as a result of human activity, of substances, heat or noise into the air, water or land which may be harmful to human health or the quality of the environment, result in damage to material property, or impair or interfere with amenities and other legitimate uses of the environment" (c.f. Art. 2.2). To achieve its goal, the Directive lays down measures "to reduce emissions in the air, water and land from the above-mentioned activities, including measures concerning waste" (c.f. Art. 1). "Best available techniques" should be applied, in which "available techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions". Summarising the provisions of the IPPC-D it can be concluded, that the identification of BAT for the non-ferrous metal industry requires an investigation of the underlying production systems with particular respect to the emission of substances, heat, and noise caused by the system into the environmental media air, water, and land. Furthermore the considerations of Annex IV, IPPC-D, have to be taken into account, in particular the requirements of Annex IV.9 (consumption and nature of raw materials and energy efficiency of the processes).

Chapter 2 of the study gives a short description of processes and techniques applied in the production of non-ferrous metals and the most common inputs, outputs and emissions. The basic description in this chapter is divided into two sections dealing with the production of zinc (2.2.1) and the production of lead (2.2.2). Due to the high level of integration in the non-ferrous metal industry, a distinction between primary and secondary processing is difficult and cannot always be kept up. Furthermore, this report deals only with those steps of non-ferrous metal production which are normally carried out at the plant site: the preparation and handling

of raw materials, the smelting or the hydrometallurgical treatment of the input charge and the refining of the raw metal produced.<sup>6</sup>

For zinc and lead industry, processing of the semi-finished or finished products such as rolling or the production of alloys, for example in the brass industry as well as operations carried out before the raw materials are delivered to the plant site such as extraction, concentration and flotation, are not covered by this document.

## **2.2 Basic description of zinc and lead production**

### **2.2.1 Zinc production**

Zinc is produced world-wide from different primary and secondary raw materials. Various hydrometallurgical and pyrometallurgical processes are in use. The choice of a production process is mainly dependent on the type of raw material available. For pyrometallurgical zinc production, for example, concentrates with a lower zinc content or a higher fluorine content are more suited. The primary processes mainly use sulphidic concentrates with a zinc content of 50 - 55 %, while secondary processes employ recycled oxidised and metallic products, mostly from other metallurgical operations. Nowadays, a clear distinction between primary and secondary zinc production is becoming more and more difficult, as most plants use both, primary and secondary raw materials. For the hydrometallurgical production of zinc, mainly processes based on electrolysis are operated on an industrial scale. Regarding pyrometallurgical zinc smelting processes, today the Imperial Smelting Process (ISP) has replaced nearly all other pyrometallurgical processes, like horizontal retorts. Zinc production from secondary materials becomes as significant as for other non-ferrous metals, despite the fact that zinc is used in a great number of various applications which result in a rather complex life cycle. In general, the processes used for the recycling of secondary zinc are pyrometallurgical processes and they can be distinguished according to the kind of raw materials employed like oxidic or metallic fractions [72]. In Germany, the processes for the recovery of zinc from secondary materials are the waelz kiln process, the ISP, remelting and the New Jersey retorts.

In the following, a short description of the common zinc production routes is given to provide a general overview. In addition, the potential sources of emissions into the air, the potential sources of water pollution as well as the main outputs are described. More detailed information can be found in literature, for example [29], [65], [66], [112]. To follow the scope of the study, emphasis is given to processes operated in German plants. Finally an overview of the main German plants is given.

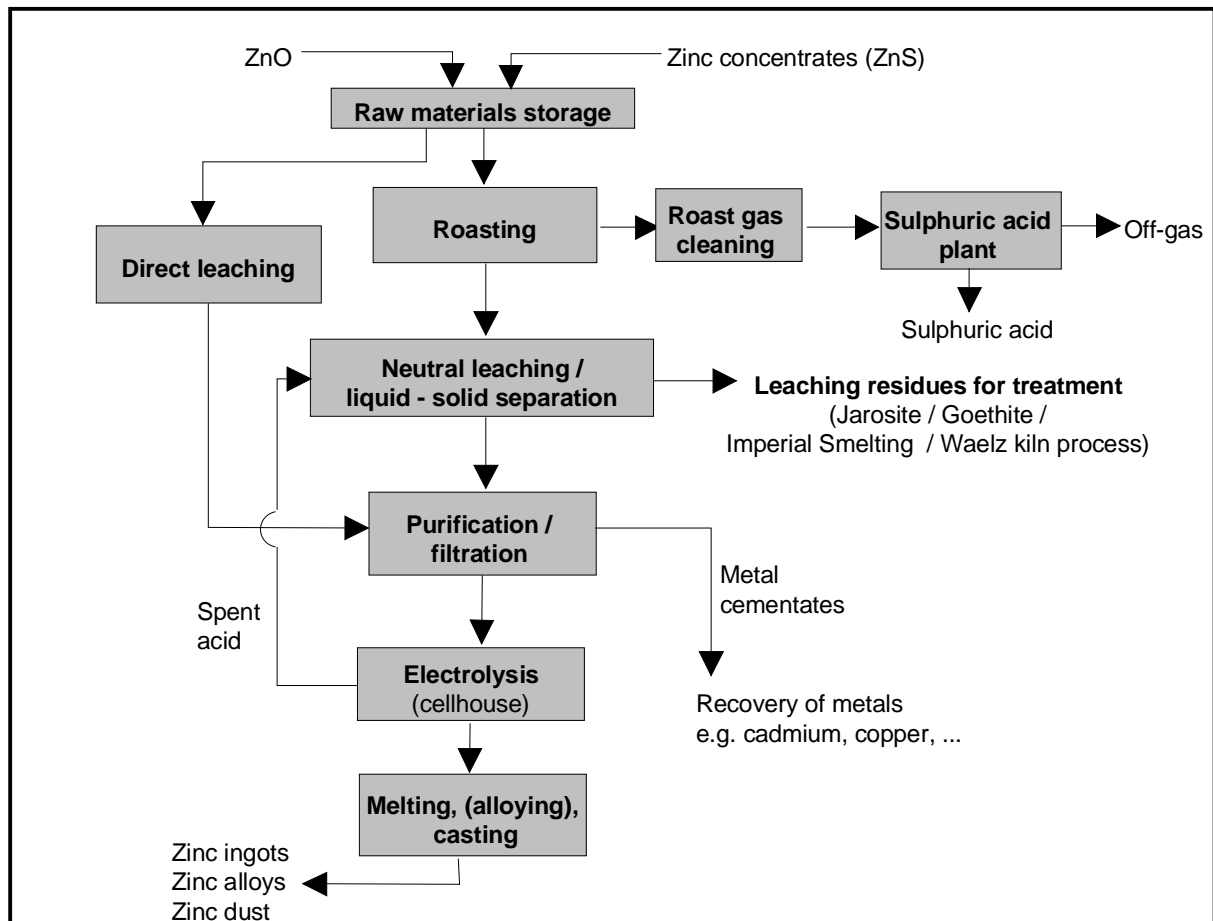
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<sup>6</sup> Mining and processing of ores are no more carried out in Germany. Furthermore, these processes are applied at very few sites in the EU only.

### 2.2.1.1 Hydrometallurgical zinc production

#### 2.2.1.1.1 General process description

The electrolytic production of zinc from a solution of zinc sulphate in diluted sulphuric acid is the predominate production process for zinc today with a share of 80 % of the total zinc production world-wide<sup>7</sup>. A typical process scheme of an zinc electrolysis is given in Figure 2-1.



**Figure 2-1: Electrolytic zinc production process**

Source: according to Osparcom [23]

It consists of the following stages:

- roasting of concentrates,
- leaching/solid-liquid separation,
- purification/filtration,
- electrolysis, and
- melting, alloying and casting.

<sup>7</sup> In the EU (world-wide) 10 (23) zinc electrolysis plants are operated.

The main other production related units of an electrolytic zinc production site are the storage, the roast gas cleaning, the sulphuric acid plant, the treatment of the mainly iron and zinc containing leaching residues, and the central water treatment plant.

In Germany mainly sulphidic zinc (zinc blende ( $\text{ZnS}$ )) concentrates (upgraded sulphidic ores with a zinc content up to 60 %) are used as raw materials. Most concentrates are imported from Scandinavia, Ireland, North and South America, as well as Australia and are transported by ship or train to the production site. Other zinc-containing materials like leached waelz oxide or filter dusts are processed to a minor extent. On the plant site, the main preparation steps are sampling, weighing and mixing of different types of concentrates. From the *raw materials storage* the concentrates are transferred to the *roasting furnace*. For roasting in zinc electrolysis plants, fluidised bed roasters are used. The concentrates are fed into the roasting furnace via a feed belt conveyor and react at temperatures around  $950^{\circ}\text{C}$  with atmospheric oxygen contained in the roasting air. Zinc blende is converted to zinc oxide ( $\text{ZnO}$ ); the residual sulphur content in the calcine should be less than 1.5 % [29].

The roast gas containing about 5 - 15 % sulphur dioxide is passed to the *roast gas cleaning* unit. The gas has to be cooled and cleaned efficiently before it is processed in the *sulphuric acid plant*. For gas cleaning a combination of cyclones, ESP and scrubbers is used [65]. For the removal of mercury from the roast gas, dry and wet methods exist. For *neutral leaching* the roasted concentrates are leached in sulphuric acid, so that most of the zinc is dissolved and the impurities such as iron, arsenic, antimony remain unsolved. Thereby a solution of zinc sulphate is formed, which has to be separated from the unsolved impurities by solid-liquid separation for further purification.

A remarkable amount of zinc is still contained in the leaching residues (zinc content up to 20 %), which can be further treated to increase the yield of zinc and other valuable metals. The *treatment of leaching residues* on an industrial scale can be done by the Jarosite, the Goethite, the Imperial Smelting or the waelz kiln process<sup>8</sup>. The *Jarosite process* starts with a hot acid leaching stage for the zinc-rich residue, so that a solid residue containing any lead and silver present can be separated. In a subsequent residue processing step, a lead-silver concentrate is obtained, which can be further processed in lead smelters. After a pre-neutralisation step with calcine and another solid-liquid separation step, the dissolved iron is precipitated by the addition of alkali compounds as hydrated alkali-iron sulphate. For the *Goethite process*, the first stages are the same as for the Jarosite process. Then zinc concentrates are added to treat the hot leach. After the reduction of iron and the precipitation of sulphur, careful iron oxidation with addition of oxygen and neutralisation leads to the

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<sup>8</sup> For each of these processes different variants exist which can deviate in detail from the general process description given. The Jarosite process used in 14 of 23 plants world-wide is the most important of these processes.

separation of Goethite. The treatment of the leaching residues in the Imperial Smelting process and the waelz kiln process is described in sections 2.2.1.2.1 and 2.2.1.2.2.

With the *purification and filtration* of impure zinc sulphate solution, nobler metal impurities are removed by cementation e.g. precipitating pure metals by adding zinc dust. Cadmium, copper and cobalt can be recovered. For the production of pure zinc metal, the purified solution is passed forward to the *electrolysis* cells. By treatment with direct electric current, pure zinc is deposited on aluminium cathodes and removed by stripping the cathodes every day. Atmospheric air coolers are used to cool down the electrolyte. To avoid emissions, the cooling towers are equipped with demisters. With *melting, alloying and casting* the zinc cathodes are transformed into different zinc product qualities and shapes. For melting, low frequency induction furnaces are used. In order to prevent particulate emissions into the air, abatement measures are applied. The recovery of cast zinc is 97.5 - 98.4 %, while the arising dross is usually returned as input material to the roaster. The zinc produced should have a purity of 99.99 % and above.

#### ***2.2.1.1.2 Main outputs and environmental concerns of the hydrometallurgical zinc production processes***

The potential sources of controlled and fugitive emissions into the air from hydrometallurgical zinc production and arising contaminants are summarised in Table 2-1.

**Table 2-1: Potential sources of controlled and fugitive emissions from German hydrometallurgical zinc production plants**

Process unit	Operation/source	Emission/main contaminants	f	c
Raw materials storage	Handling, storage, transport	Dust	x	
Roasting/roast gas cleaning	Leaks, cleaning operations	Gas, dust, inorganic volatiles	x	
Sulphuric acid plant	Off-gas from acid plant	Gas, mist		x
	Leaks	Gas, mist	x	
Neutral leaching/ treatment of leaching residues	Transport/handling of calcine; handling of reagents	Dust		x
	Leaching	Mist		x
Purification	General operation	Gas, mist		x
Electrolysis	Electrolysis cells	Mist		x
	Cooling tower	Mist		x
Melting, alloying, casting	Material handling, off-gas from furnaces	Dust, fumes		x

f: fugitive emissions; c: controlled emissions

Source: partly according to Osparcom [65]

To minimise fugitive emissions general rules should be applied [65]. The total emissions into the air from roasting, the roast gas cleaning and the sulphuric acid plant are nowadays very low, except for sulphur dioxide and sulphuric acid mist. The potential sources of water pollution are summarised in Table 2-2.

**Table 2-2: Potential sources of water pollution from German zinc electrolysis plants**

Process unit	Operation/source	Use options
Roasting/roast gas cleaning	Wet cleaning of roast gases	Waste water treatment plant
Leaching	General operations including wet gas cleaning	Return to leaching
Purification	General operations	Return to leaching
Electrolysis	Cleaning of cells, anodes and cathodes	Return to leaching
All process units	Maintenance	Waste water treatment plant
Waste water treatment plant	Effluent treatment	Discharge

Source: partly according to Oskarcom [65], European Community [23]

The waste water treatment is based on a combination of neutralisation and precipitation processes. The content of lubricants should be removed prior to further treatment [65]. The main residues generated in hydrometallurgical zinc production depend upon the process used for the treatment of leaching residues. No recycling option exist for the iron containing residues Jarosite, and Goethite, so that dumping remains the only feasible option. The use of haematite as raw material for ironmaking in integrated steel plants is restricted by the content of impurities like sulphur or zinc [67]. The lead-silver by-product can be used as secondary raw material for lead production plants. The outputs and the use/treatment options are summarised in Table 2-3.

**Table 2-3: Potential outputs from German zinc electrolysis plants**

Process unit	Output	Use/treatment options
Electrolysis	Electrolytic zinc	Main product
Sulphuric acid plant	Sulphuric acid	Sale product
	Sludge	Dumping
	Calomel	Sale product
Leaching	Lead-silver by-products	Recovery of metals
Purification	Metallic cementates	Recovery of copper, cadmium, cobalt, thallium (internal or external)
Treatment of leaching residues	Jarosite Zinc-iron intermediate	Land disposal Imperial Smelting process/waelz kiln process
Waste water treatment plant	Sludges/residues	Recovery of metal content (internal), land disposal, sale product

Source: partly according to Oskarcom [65]

## 2.2.1.2 Pyrometallurgical zinc production

### 2.2.1.2.1 Imperial Smelting Process

#### *General process description*

The pyrometallurgical Imperial Smelting Process (ISP) for the simultaneous production of zinc and lead in a lead-zinc shaft furnace was developed in the UK in the late forties and fifties. A first ISP plant was operated in the early sixties (c.f. [65], [29]). Today, 12 ISP plants exist world-wide with 4 plants operating in the European Union. Their production amounted to 867,000 tons of zinc and 364,000 tons of lead bullion in 1994, i.e. approximately 12 % and 7 % of the total world production of these metals respectively [54]. The data given in Table 2-4 show improvements in process technology and plant performance over recent decades.

**Table 2-4: Data on ISP plant performance**

<b>IS Plant (cross section of the furnace: 17.2 m<sup>2</sup> (standard size))</b>		
Year	<b>1963</b>	<b>1990</b>
Zinc production [t/a]	35,000	90,000
Zinc yield [wt.-%]	91.7	95.5
Lead production [t/a]	17,000	40,000
Lead yield [%]	94	95
Pb/Zn ratio in charge material	0.49	0.4 - 0.6

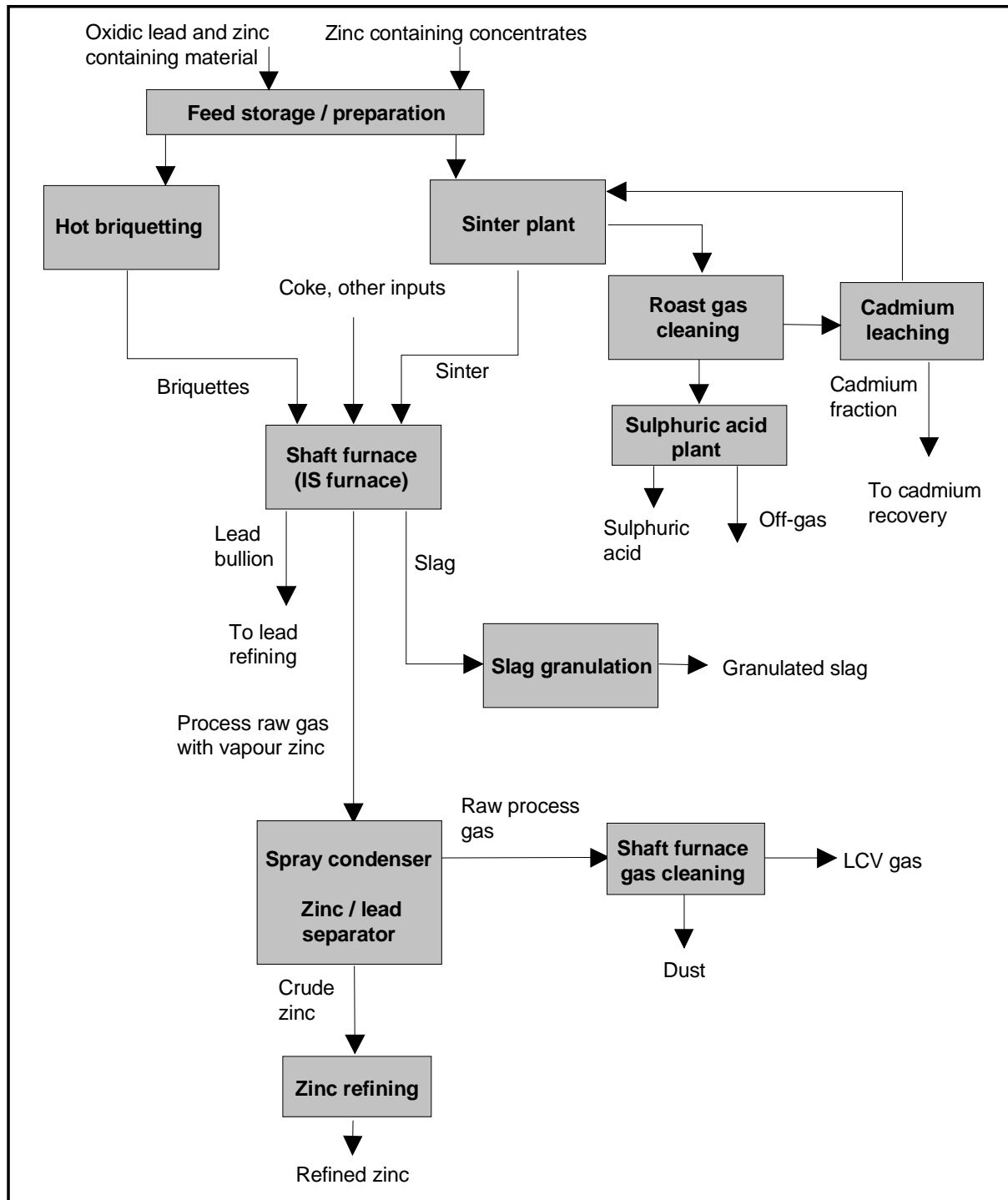
Source: Graf [29]

In general an ISP plant can be subdivided into process units:

- sinter roasting of raw materials in the sinter plant,
- hot briquetting of raw materials,
- smelting of the charge in a blast furnace,
- thermal zinc refining, and
- casting.

The main other production related units of an ISP plant are the feed storage area, the roast gas cleaning and cadmium leaching plant, the sulphuric acid plant, and the central water treatment plant. A typical process scheme is given in Figure 2-2. The main advantage of the ISP is its ability to treat a wide range of zinc-bearing materials. Zinc, lead or mixed zinc/lead ores and concentrates as well as secondary materials like zinc-lead oxides, zinc ashes, zinc containing batteries, and EAF dusts can be processed that would otherwise cause severe problems e.g. in electrolytic zinc production. Raw materials like ore concentrates are desulphurised and agglomerated in the *sinter plant*. The sinter roasting line consists of a slow forward moving roaster. To remove the sulphur the charge is placed on the sinter machine and ignited. The combustion air is blown from below through the line. Sulphur and impurities like cadmium, mercury and chlorides are removed by vaporisation. The roaster gases are collected and

treated in the *roast gas cleaning* system. Due to the high temperatures on the line (the operation temperature in the sintering zone is about 1,200°C [29]), the charge is agglomerated.



**Figure 2-2: Imperial Smelting process for zinc production**

In addition, some of the ISP plants have their own agglomeration plant for *hot briquetting* of finer oxidic raw materials, like zinc ashes. These materials are preheated in a furnace and briquetted at temperatures around 300°C. Due to the temperatures chosen, organic substances



like PCDD/PCDF can be vapourised and will be captured in special filters [48]. After breaking and screening, the sinter is charged together with the briquettes with preheated coke in alternating layers at the top of the furnace. Typically, a sinter consists of 30 - 50 % zinc, 10 - 25 % lead, and less than 1 % sulphur depending on the raw materials processed. The aggregates for sinter cooling, breaking, and sieving are encapsulated, the captured off-gases are dedusted in fabric filters.

Preheated air (about 1,100°C) is blown from below in the *shaft furnace (IS furnace)* through tuyères. The coke is converted into carbon monoxide which reacts with the zinc oxide in the charge. Together with the process gases, evaporated zinc metal as well as cadmium and some lead leave the furnace with temperatures of about 1,000°C. To condense the zinc, these process gases are passed to a *spray-condenser* which uses a shower of metallic lead. After the condenser, the process gases with their high carbon monoxide content are cleaned with a wet scrubber (*shaft furnace gas cleaning system*) and later used for e.g. preheating process air or coke. From the condenser the molten lead enriched with zinc is pumped into a cooling launder, where the solubility of the zinc is decreased. Zinc metal separates and two layers of molten metals are obtained. The raw zinc can be separated from the lead in the *zinc/lead separator* for refining. The liquid lead is recirculated to the condenser. In the zinc *refinery*, a thermal refining of zinc is carried out by fractionated distillation. Impurities like lead, cadmium and iron have to be removed.

Lead bullion and slag are tapped at the bottom of the furnace and separate by gravity in a forehearth. The slag is granulated with water. Off-gases from slag granulation can be captured and cleaned using a wet scrubber or wet ESP.

For *roast gas cleaning* different gas cleaning techniques can be used. A typical gas cleaning unit consists of a hot ESP, a gas washer for cooling, a first wet ESP, mercury washing tower (Boliden/Norzink mercury removal process), and a second wet ESP. Most of the cadmium contained in the off-gas can be found in the ESP dust. To prevent cadmium enrichment by recirculation of sinter dust, the arising dusts are treated in a *cadmium leaching* stage. Cadmium can be recovered as metal or cadmium carbonate. After cleaning, the off-gas is fed to a *sulphuric acid plant* for sulphur dioxide conversion.

### ***Main outputs and environmental concerns of Imperial Smelting plants***

The potential sources of controlled and fugitive emissions into the air from ISP plant operation and contaminants are summarised in Table 2-5.

**Table 2-5: Potential sources of controlled and fugitive emissions into the air from the German ISP plant**

Process unit	Operation/source	Contaminants	f	c
Feed storage	Handling, transport, storage	Dust	x	
Sinter plant	Hood, sinter classification	Gas, dust		x
	Feed and product transport systems, bins	Dust	x	x
Hot briquetting plant	Agglomeration	Gas, dust, volatiles		x
Roast gas cleaning	Leakages	Gas, dust, inorganic volatiles	x	
Sulphuric acid plant	Off-gas from acid plant	Gas, mist		x
	Leakages	Gas, mist	x	
IS furnace	Insufficient exhaustion, leakages	Gas, dust	x	
	Transport/storing/charging of hot sinter and coke	Dust, gas		x
	General ventilation, Zn-separation, tapping (lead/slag)	dust		x
	Pre-heating of air and coke; LCV gas combustion	Gas, dust		x
Slag granulation	Granulation	Dust, mist, gas		x
Zinc refinery/casting	Insufficient exhaustion, leakages	Dust	x	
	Hoods from furnaces, heating gases from furnaces/distillation columns	Dust, inorganic volatiles		x

f: fugitive emissions; c: controlled emissions

Source: partly according to Osparcom [65], HMIP [30]

The potential sources of water pollution are summarised in Table 2-6.

**Table 2-6: Potential sources of water pollution from the German ISP plant**

Process unit	Operation/source	Use options
Feed storage	Surface water (rain/wetting)	Waste water treatment plant
Sinter plant	Scrubber (sinter fine cooling)	Waste water treatment plant
Roast gas cleaning	Wet gas cleaning	Waste water treatment plant
Cadmium leaching	Cadmium leaching	Waste water treatment plant
IS furnace	Gas cleaning	Waste water treatment plant; recirculation
	Gas cleaning coke heating chamber	Recirculation
Slag granulation	Granulation waste water	Recirculation, waste water treatment plant
	Wet gas cleaning	Recirculation, waste water treatment plant
Waste water treatment plant	Effluent treatment	Discharge

Source: according to Osparcom [65], HMIP [30]

Nearly all plants use internal water recirculation for cooling water and the re-use of waters as well as a *central waste water treatment* plant. Specific waste water streams or effluents might be pre-treated [65].

Lead bullion tapped from the *IS furnace* has to be refined to recover the content of copper, silver, gold. Depending on the market conditions, the cadmium fractions obtained in the *cadmium leaching* unit can be sold [65]. According to [65], cadmium cementate can be refined and marketed as cadmium metal; cadmium carbonate can be sold for metal recovery or has to be dumped. After treatment in the *slag granulation*, IS furnace slag can be used as road construction material. Sludges arising from the *central water treatment* plant are usually recycled to the production process.

**Table 2-7: Output from the German ISP plant**

Process unit	Output	Use/treatment options
IS furnace	Lead bullion	Lead refining
Slag processing	Granulated slag	Road construction material
Cadmium leaching	Cadmium fraction	Cadmium recovery
Zinc refining	Zinc Refining dross Hard zinc Cadmium-zinc alloy Liquation lead	Main sale product Internal recycling Internal recycling Cadmium recovery Internal recycling
Waste water treatment plant	Sludges/residues	Recycling to sinter plant for metal recovery
Sulphuric acid plant	Sulphuric acid	Sale product
	Mercury containing residue	Dumping

Source: partly according to Osparcom [65]

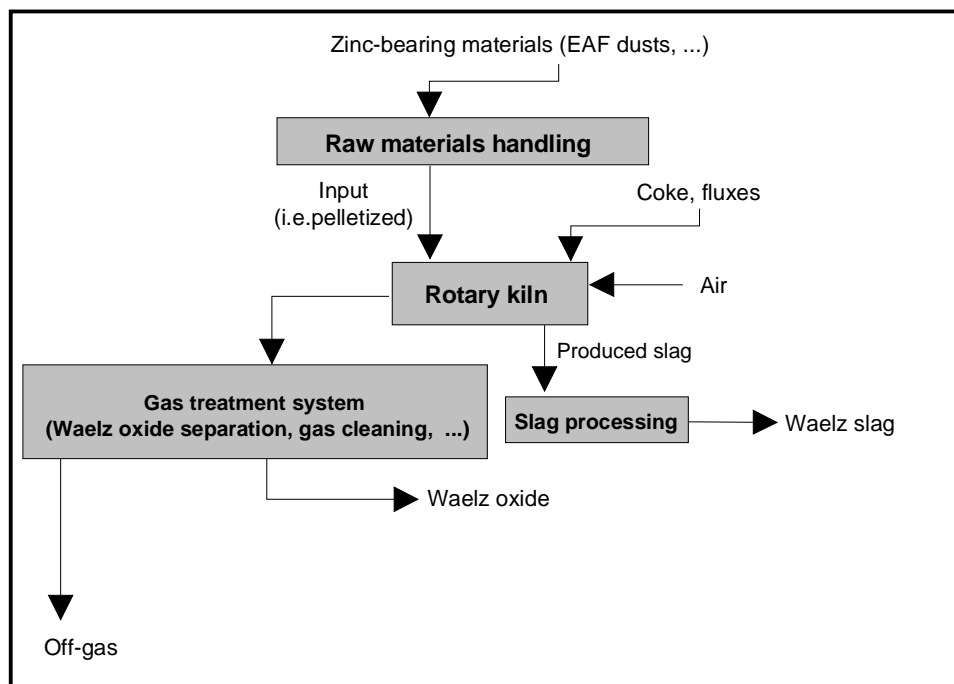
### 2.2.1.2.2 Waelz kiln process

#### General process descriptions

Originally in the 20<sup>th</sup> of this century, the waelz kiln process<sup>9</sup> was used for the treatment of low-grade oxidic ores to obtain zinc oxide suitable for further smelting. In the meantime, it has been mainly used as an enrichment process for the treatment of secondary raw materials e.g. poor oxidic residues and oxidic dusts. Treatment of dust from electric arc furnaces (EAF) in the iron and steel industry began in the late 70<sup>th</sup> and is now the predominate application not only in Germany. In general, a waelz kiln plant can be subdivided into three main process units:

- raw materials handling,
- rotary kiln, and
- gas cleaning units

Main other production related units of the waelz kiln plant are slag treatment and waelz oxide treatment. A typical process scheme is given in Figure 2-3.



**Figure 2-3: Waelz kiln process**

In general, the handling of raw materials is depending on the raw materials processed and the equipment used and can therefore differ from site to site. For example, EAF dust is delivered to the waelz plants operated by companies Z4 and Z5 in pelletized form or as dry filter dust, while at the other plant (company Z7) no dry EAF dust is processed. The raw materials

<sup>9</sup> More detailed information on the waelz kiln process can be found in literature, for example in [29] and [32].

handling at the waelz plant operated by the companies Z4 and Z5 include a mixing and pelletizing step. Dry dust and coke fines are unloaded by pneumatic transport to silos. The materials are mixed and pelletized before the material is sent directly to the feeding system or for intermediate storing. In the raw materials storage and preparation unit, the materials are fed by a shovel loader to a central feeding hopper and transported to the different production bins. Through weighing feeders the charge is reclaimed and carried by conveyor belts to the feeding pipe at the upper end of the kiln. The quantity of reduction materials (coke) according to the zinc content of the raw materials and fluxes for the desired slag quality can be controlled by weighing equipment. In the slowly rotating rotary kiln (about 1 - 1.2 rpm) the solid materials are first dried and then heated up by the hot gas, which passes counter-currently through the kiln, and the contact with the refractory lined walls. A typical kiln is about 40 - 50 m long, has a free diameter of about 2.60 - 3.60 m and is slightly inclined.

The normal operation temperature inside a waelz kiln is about 1,200°C. Depending on technical kiln parameters like inclination, length and rotation speed the material has an average residence time between 2 - 4 hours. In the strongly reducing atmosphere of the solid bed, zinc, lead and other heavy metals are reduced. Zinc and lead are evaporated into the gas atmosphere. Chlorides and partly alkalines, depending on the slag basicity are evaporated together with the heavy metals. Due to a surplus of air, the metal vapours are (re-) oxidised to metal oxides in the atmosphere. The mixed oxides are drawn from the kiln with the process gases and separated in the gas treatment system. Typically a settling chamber for removal of coarse dust, a cooling step for gas cooling and a final bag house filter are operated. Different options for further processing of the obtained waelz oxide exist. It can be compacted by hot briquetting or sintering and sold to pyrometallurgical zinc-producing plants like Imperial Smelting Process plants. If the lead oxide content is too high, a calcination step to volatilise the lead mainly as lead chloride can be applied. A new technology for upgrading the waelz oxide, waelz oxide leaching, allows a further processing of waelz oxide in zinc electrolysis (c.f. Section 3.1.2.2). The slag produced in the kiln is discharged continuously from the kiln end. After cooling, screening and crushing, the slag can be used as a secondary recycling product. Applications are the civil engineering especially for road construction as undersurface layer, filler or bound with bituminous as surface layers. In addition, the slag is suitable as a flux for cement clinker production or as an iron source in the iron and steel industry.

### ***Main outputs and environmental concerns of waelz kiln plants***

In Table 2-8 potential sources of controlled and fugitive emissions from the waelz kiln are shown.

**Table 2-8: Potential sources of controlled and fugitive emissions from German waelz kilns**

Process unit	Operation/source	Contaminants	f	c
Feed storage and preparation	Stockpiling, handling, charge preparation	Dust	x	
	Hopper exhaust filter	Dust		x
Waelz kiln	Furnace mouth	Dust		x
Gas cleaning system	Off-gas from gas cleaning/volatile adsorption	Dust, volatiles		x
Slag processing	Cooling, granulation	Dust, mist		x

f: fugitive emissions; c: controlled emissions

Main outputs from the German waelz plants are summarised in Table 2-9.

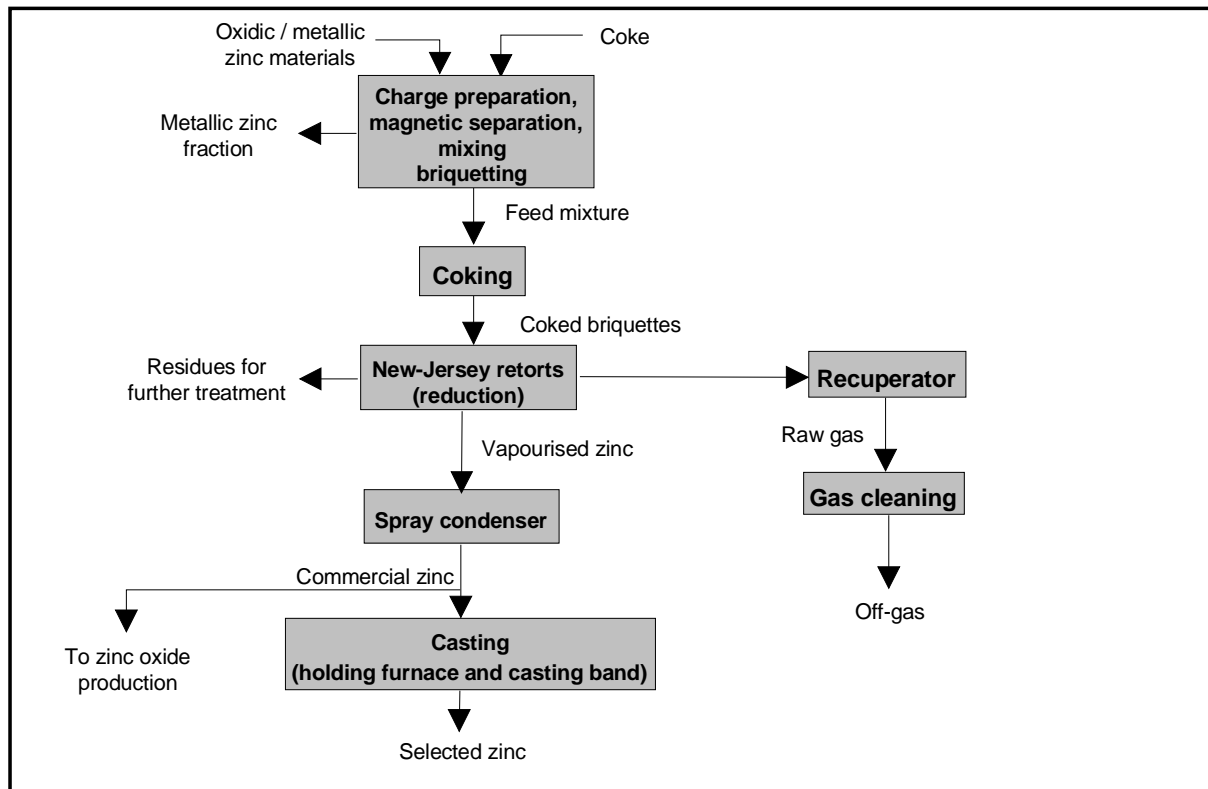
**Table 2-9: Potential outputs from German waelz plants**

Process unit	Output	Use/treatment options
Gas treatment system	Waelz oxide	Sale product
	Loaded adsorbent	Dumping
Slag treatment	Slag	Civil engineering/road construction
Waelz oxide leaching	Double leached waelz oxide	Sale product
	Sludges	Internal recycling

### 2.2.1.2.3 Reduction in vertical retorts (New Jersey retort process route)

#### General process description

In vertical retorts, a large variety of oxidic and metallic secondary materials are processed simultaneously. A schematic diagram of the New Jersey retort process route is shown in Figure 2-4. The *charge preparation* includes crushing, sieving, the separation of oxidic and metallic fraction, and dechlorination, if necessary. The oxidic materials are mixed with bituminous coal. Subsequently, the mixture is briquetted together with a binding agent, coked at temperatures around 800°C in an autogeneous *coking* furnace, and charged into the top of the *New-Jersey retorts*. The core of the furnace is an indirectly heated retort made of silicon carbide. By external heating with natural gas and carbon monoxide recovered from the retort process, temperatures of about 1,200°C are achieved. Zinc oxide is reduced and zinc is vaporised. Subsequently, the zinc vapours are quenched in a spray condenser and collected as liquid zinc at a temperature of 500°C. The processed zinc is mainly transported in ladles to the zinc oxide production plant, a small quantity is *cast* in ingots. The remaining carbon monoxide-rich process gas is cleaned by scrubbing and then used internally, e.g. for heating the retorts. After zinc extraction, the residues of the briquettes are discharged as retort residue from the bottom of the retort for further treatment i.e. recovery of metals and energy from carbon contained.



**Figure 2-4: Vertical retort process route**

#### 2.2.1.2.4 Fuming plant

Fuming is a thermal concentration process for lead and zinc-containing slags and residues [29]. It is used for the removal of zinc (and lead) from fluid phases e.g. liquid slag. The mixed zinc-lead oxide obtained has a low content of chlorine and can be used for further metal production. Other outputs are slag, small amounts of matte and steam, generated by indirect cooling of the production aggregates.

A fuming plant is operated by company Z6 since 1996 and is described in Section 3.1.2.3 in detail.

#### 2.2.1.2.5 Melting of metallic raw materials

Whereas the recycling of oxidic zinc containing materials is done in the above mentioned processes (e.g. the waelz kiln), for recycling of metallic residues mainly induction type or muffle type furnaces are operated. After the metallic materials have been melted and liquated, the produced zinc can be separated from the dross, cast and transferred for further refining.

#### **2.2.1.2.6 Refining of crude zinc**

Crude zinc produced by the pyrometallurgical processes contains several impurities as lead, iron, cadmium, or arsenic depending on the production process and the raw materials processed. To obtain the commercial grades, a further purification step is necessary. After liquation, further refining of crude zinc is nowadays carried out by two-stage distillation in high-temperature distillation columns, a process developed by the New Jersey Zinc Co. Detailed information can be found in [29]. The main process steps are:

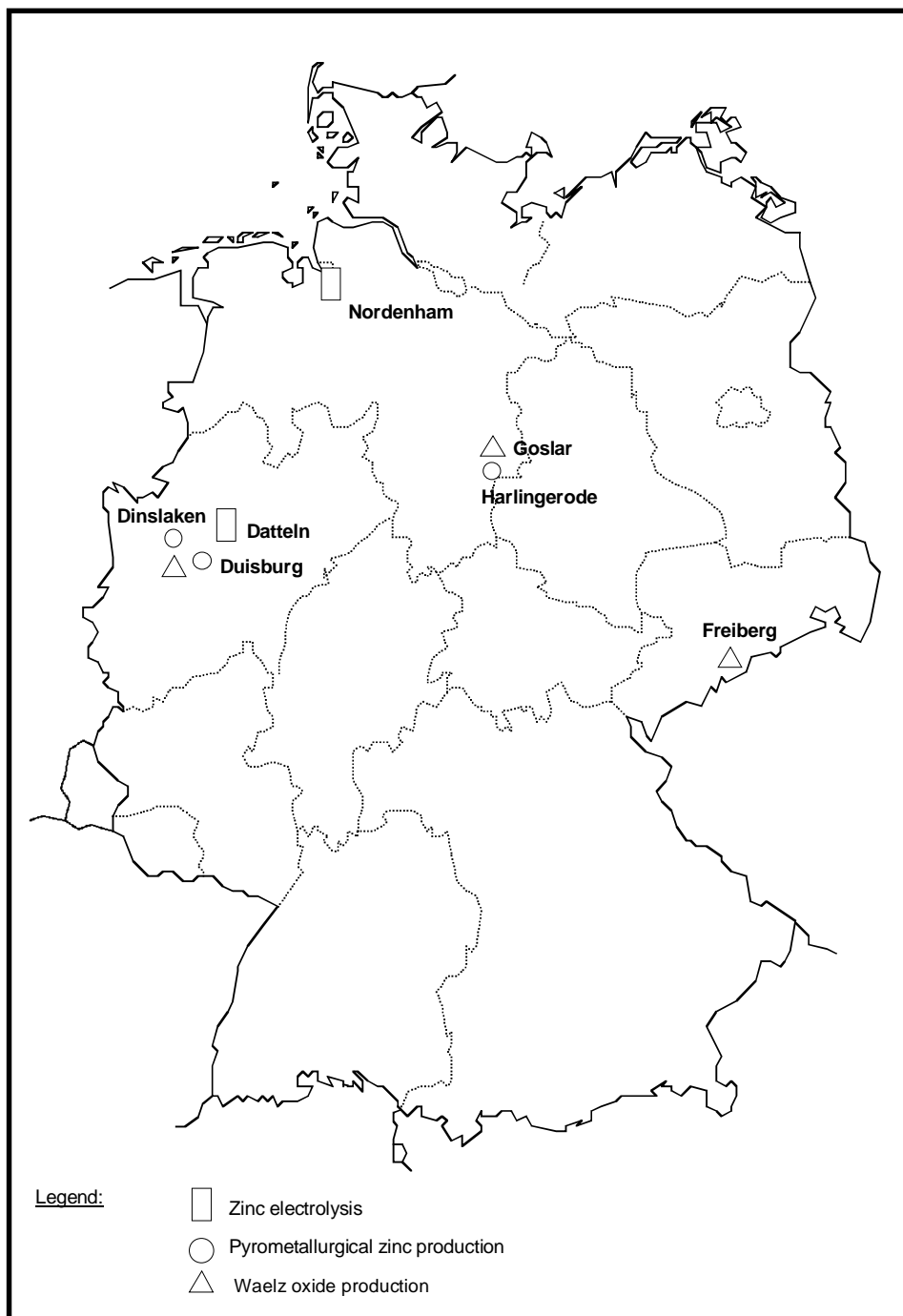
- melting of crude zinc in a feeding furnace,
- evaporation of cadmium and part of the zinc in a first distillation column with subsequent condensation, and
- separation of pure zinc metal (SHG grade) in a second column with a zinc-cadmium alloy as a second product.

The zinc-cadmium alloy can be treated for pure cadmium recovery. The cadmium-free zinc fraction from the underflow of the first column is liquated to separate impurities.

#### **2.2.1.3 Zinc production plants in Germany**

In Germany, two primary plants are based on the hydrometallurgical electrolysis process route, whilst a third one operates on the basis of the Imperial Smelting process. Three further plants operate a waelz kiln, while at one site the New-Jersey retort process route in combination with a fuming plant is used. At several sites, remelting of zinc scrap is done. The locations of the main zinc production plants in Germany are shown in Figure 2-5.





**Figure 2-5: Location of zinc production plants in Germany**

**Table 2-10: Main zinc production and recycling plants in Germany**

	<b>Metaleurop Weser Zink GmbH, Nordenham</b>	<b>Ruhrzink GmbH, Datteln</b>	<b>Metallhütte M.I.M. Hüttenwerke Duisburg</b>	<b>B.U.S. Metall GmbH, Duisburg</b>	<b>B.U.S. Zinkrecycling Freiberg GmbH</b>	<b>Harzer Zink GmbH, Harlingerode</b>	<b>Harz Metall GmbH, Goslar</b>	<b>Metallwerk Dinslaken</b>
Process technology	Electrolysis	Electrolysis	Imperial Smelting process Thermal refining	Waelz process	Waelz process, Waelz oxide leaching	New-Jersey retorts Fuming plant Induction furnace	Waelz process	Remelting
Feed consumption [t/a] / composition	225,000 concentrates	170,000 concentrates	250,000 with 50 % secondary materials	60,000 mainly EAF dust	40,000 mainly EAF dust	60,000 secondary materials	65,000 57 % EAF dust 43 % retort residue	45,000 mainly zinc scrap
Zinc production capacity [t/a]	130,000	105,000	100,000	12,000 (zinc content waelz oxide)	9,000 (zinc content waelz oxide)	20,000 HG zinc 6,500 remelted zinc	9,500 (zinc content waelz oxide)	40,000
Main products	Zinc and zinc alloys	Electrolytic zinc	Zinc and zinc alloys Lead bullion	Waelz oxide	Leached waelz oxide	High grade zinc	Waelz oxide	Zinc and zinc alloys
Main by-products	Sulphuric acid Cadmium	Sulphuric acid	Sulphuric acid Cadmium carbonate IS furnace slag	Slag	Slag	Slag Mixed oxide	Slag	Zinc ashes
Certificates	ISO 9002	-	-	-	-	ISO 9002	n. a.	-

## 2.2.2 Lead production

Lead is produced from various primary and secondary raw materials. As main primary raw material, sulphidic lead ore concentrates are used. Besides used lead-acid batteries, which are the most important secondary raw material, recycled oxidised and metallic products, mostly from other metallurgical operations are processed. A clear distinction between primary and secondary lead production processes is often difficult, as many plants use both primary and secondary raw materials<sup>10</sup>. On an industrial scale, only pyrometallurgical processes are operated for lead production; hydrometallurgical production of lead is not done on a commercial scale up to now. In the following, a general overview of the type of raw materials processed and the most common processes for lead production is given. In addition, the potential sources of emissions into the air, the potential sources of water pollution as well as the main outputs are described. More detailed information can be found in literature, for example in [66], [74], and [83]. Within the scope of the study, the emphasis is laid on the processes applied in German plants and finally an overview of the main German lead production plants is given.

### 2.2.2.1 Lead-containing raw materials

In general, the most common feed for primary lead production are sulphidic lead concentrates which contain 60 - 70 % lead on average. Carbonatic/oxidic lead concentrates are of minor importance. Lead concentrates are obtained from lead ores recently mined with a lead content between 1 and 8 % by several beneficiation steps like crushing, separation, grinding, flotation, and drying. No more mining or ore beneficiation is carried out in Germany, so all lead concentrates processed in Germany have to be imported. Important exporting countries are Sweden, Ireland, South-America, Australia and Canada.

The predominate secondary input material for lead production are used lead-acid batteries with a world-wide portion of about 80 %. They are mainly used in cars, but there also several other types in use for emergency power supply, electric cars, load levelling, cattle-grazing, traffic lights, telephones etc. In general, three different battery types exist:

- SLI (Starting, Lighting, Ignition) batteries, of which the bulk is automotive,
- traction vehicle batteries, and
- stationary batteries for supplying emergency power mainly for commercial applications.

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<sup>10</sup> In [65], the Oslo and Paris Commissions give descriptions of *Best Available Techniques* (BAT) for the primary production of lead covering processes, equipment and management. Besides the conventional sinter plant - blast furnace route for lead production from concentrates, also new technologies are included. However, nowadays these plants claim to process a 50 % and above share of secondary raw materials. Other processes exclusively for the recycling of scrap materials (so-called secondary materials) are not covered by [65], but in the study on hand.

The key components of all these types are: a polypropylene containment box, metal grids, electrode paste, sulphuric acid, connectors and poles of lead alloy, and grid separators of PVC. In the past, grids were mainly made from antimony-lead alloys, but new trends show an increase in the usage of calcium-lead alloys. The electrode paste of used batteries is a mixture of lead sulphate and lead oxide. As an example, the composition of typical battery scrap material is given in Table 2-11.

**Table 2-11: Composition of typical lead-acid battery scrap**

Component	[wt.-%]
Lead (alloy) components (grid, poles, ...)	25 - 30
Electrode paste (fine particles of lead oxide and lead sulphate)	35 - 45
Sulphuric acid (10 - 20 % H <sub>2</sub> SO <sub>4</sub> )	10 - 15
Polypropylene	5 - 8
Other plastics (PVC, PE, etc.)	4 - 7
Ebonite	1 - 3
Others materials (glass, ...)	< 0.5
Total weight [kg]	17 - 19

Source: Behrendt/Steil [6], [7]; Steil [81]

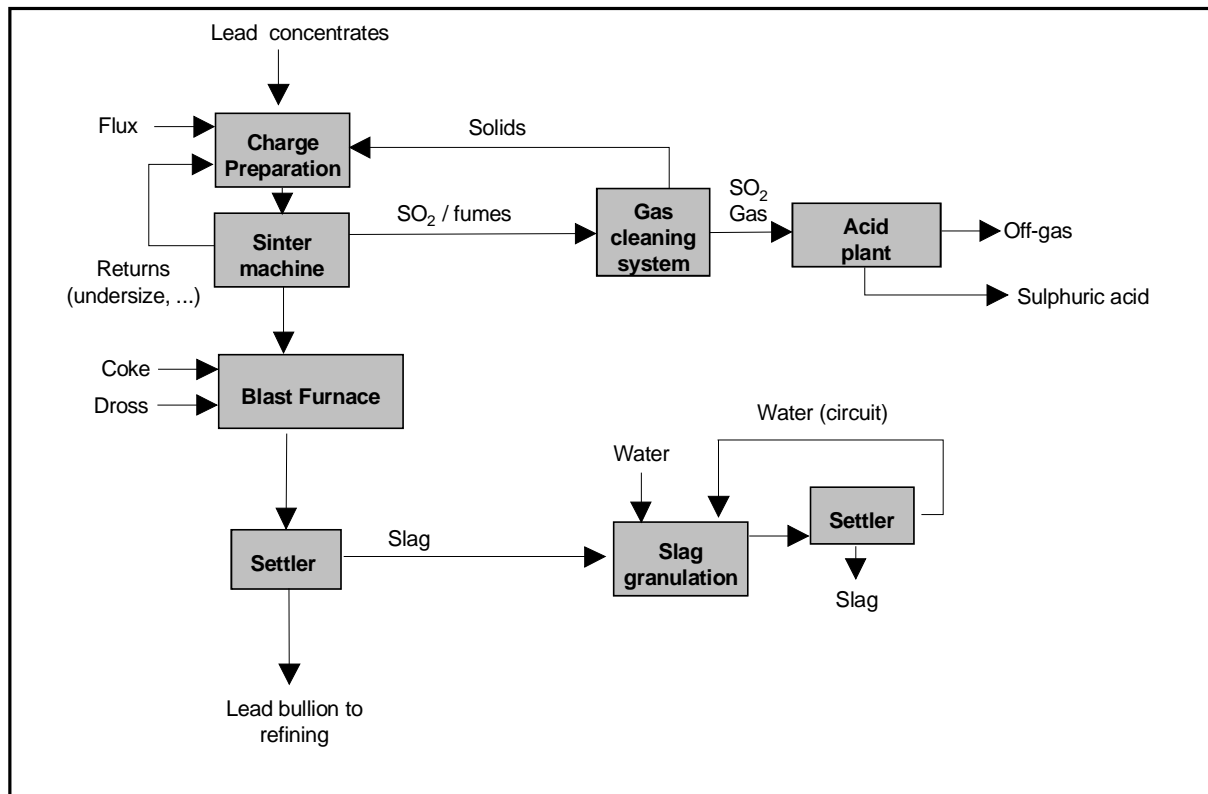
It has to be mentioned, that the composition of battery scrap varies depending from location, season and structure. In addition, the references for the total weight differ: Behrendt [7] and Steil [81] measured an average weight of 17 kg per automotive starter battery. According to Jolly [36], an average weight of only 13.5 kg per battery with a polypropylene box can be expected. For other uses the weight varies between 100 g and several tons. The share of old-styled batteries with ebonite (hard rubber) boxes is decreasing. This material contains 6 - 10 % sulphur and can therefore form sulphur dioxide by combustion. In the gas cleaning devices, the sulphur dioxide can react with lead-oxide to form lead-sulphate [7]. The transport and storage of batteries has to fulfil existing regulations e.g. the regulations for the transport of dangerous goods in Germany.

The second important secondary raw material is scrap from lead-acid battery manufacturing with a share of about 10 % [38]. Other secondary materials like metal sheets, pipe scraps, sludges and drosses are of minor importance.

#### **2.2.2.2 Sinter plant - blast furnace route for lead production**

Traditional lead production involves the sintering oxidative roast of ore concentrates in order to remove the sulphur and the subsequent blast furnace reduction of the sinter product [83]. The lead bullion obtained by this so-called conventional smelting route has to be further processed in the lead refinery (c.f. Section 2.2.2.5). A schematic view of the conventional lead smelting route is given in Figure 2-6 [23]. The generic conventional plant consists of the

installations for stockpiling and charge preparation (pre-treatment), the sinter-roasting plant with the sulphuric acid plant, the smelting part and the refinery. The smelting itself consists of the charging and feeding systems, the melting furnace, the devices for gas cleaning, gas cooling and heat recovery, and the tapping parts for the handling of molten products mainly lead bullion and slag.



**Figure 2-6: Sinter plant - blast furnace route for lead bullion production (example)**

Source: partly according to European Commission, DG XI [23]

As the last German blast furnace plant for lead production from primary raw materials<sup>11</sup> was shut down in 1995, consequently no sinter plants or blast furnaces for lead production from lead concentrates are in operation. However, the Imperial Smelting process produces lead and zinc in one single shaft furnace operation from primary and secondary raw materials. As the Imperial Smelting process is basically a zinc production furnace it is dealt with in Section 2.2.2.

<sup>11</sup> For lead production exclusively from secondary raw materials one shaft furnace plant is operated in Germany (c.f. Sections 2.2.2.4 and 3.2.2).

### 2.2.2.3 New direct smelting processes for lead production

During recent decades, several innovative new lead production processes have been developed to overcome the drawbacks of the conventional sinter plant - blast furnace route. The most promising ones are the flash smelting and the bath smelting processes, among them the QSL (Queneau-Schuhmann-Lurgi) technology, the Kivcet technology, and the TBRC process have proven their suitability on an industrial scale. The QSL process is operated in three industrial plants world-wide, located in Germany ("Berzelius" Metall GmbH, Stolberg), South Korea (Korea Zinc, Onsan) and China (CNIEC). The Kivcet process is operated in Italy (Nuova Samim, Sardinia), in Kazakhstan (UK Lead and Zinc Combine) and in Canada (Trail, British Columbia). The TBRC process (Boliden, Rönnskar) is operated in Sweden since 1976. For further processes, like the Sirosmelt technology and the Outokumpu pilot plant until now only few process data are available. An overview of the main new direct smelting processes is given in Table 2-12.

**Table 2-12: Technical data on new direct smelting process plants**

Process	Pre-treatment	Smelting/ extraction of lead bullion	Reference plants	Capacity [t/a]	Since
<b>Boliden Kaldo</b>	Drying of feed mixtures	Batch flash/bath smelting into Top Blown Rotary Converter	- Rönnskar (Sweden)	65,000	1976
<b>Kivcet</b>	Drying of feed mixtures	Continuous flash smelting	- Trail, British Columbia (Canada) - Nuova Samim (Italy) - UK LZC (Kazakhstan) 2 plants	120,000 90,000 60,000	1998 1987 1986
<b>Outokumpu</b>	Drying of feed mixtures	Continuous flash smelting	- Pilot plant only	n. a.	n. a.
<b>QSL</b>	Use of moist feed	Slag bath smelting continuous	- "Berzelius" Metall GmbH (Germany) - Korea Zinc (South Korea) - CNIEC (China)	90,000 60,000 52,000	1990 1992 1995
<b>Sirosmelt (Ausmelt/ Isasmelt)</b>	Use of moist feed	Slag bath smelting continuous/semi- continuous	- Metaleurop Weser Blei (Germany) - Mount Isa (Australia) - Northfleet (UK)	90,000 60,000 < 60,000	1996 1991 1991

The major innovation in the processes mentioned is the combination of the oxidation and the reduction stages. Compared to conventional smelting plants, these processes reduce drastically the energy consumption, the amount of off-gas to be treated, and the sulphur dioxide emissions. The resulting high sulphur dioxide concentration in the off-gas permits easily the recovery of sulphuric acid in a contact plant. Additionally the number of potential emission sources is reduced compared to the conventional sinter plant - blast furnace route. These processes are also suitable for the processing of secondary raw materials, whereby a share of

50 % and more can be achieved. At the end, these processes claim to offer capital expenditure and operating cost savings [19].

#### 2.2.2.4 Lead production from secondary raw material

Lead production from secondary materials aims to recover lead from lead-containing materials, i.e. to a large extent from battery scrap, and to a minor extent from metal sheets, pipe scraps, drosses and sludges. In the production plants, several other materials and material fractions are recovered simultaneously. In principle, secondary lead production is based on pyro- and hydrometallurgical process steps: the preparation of battery and scrap materials (c.f. Section 2.2.2.4.1), the smelting of lead-containing inputs (c.f. Section 2.2.2.4.2), the refining and alloying (c.f. Section 2.2.2.5), and further chemical and metallurgical process steps. An overview of the technical processes for lead recycling from lead-acid batteries is given in Table 2-13.

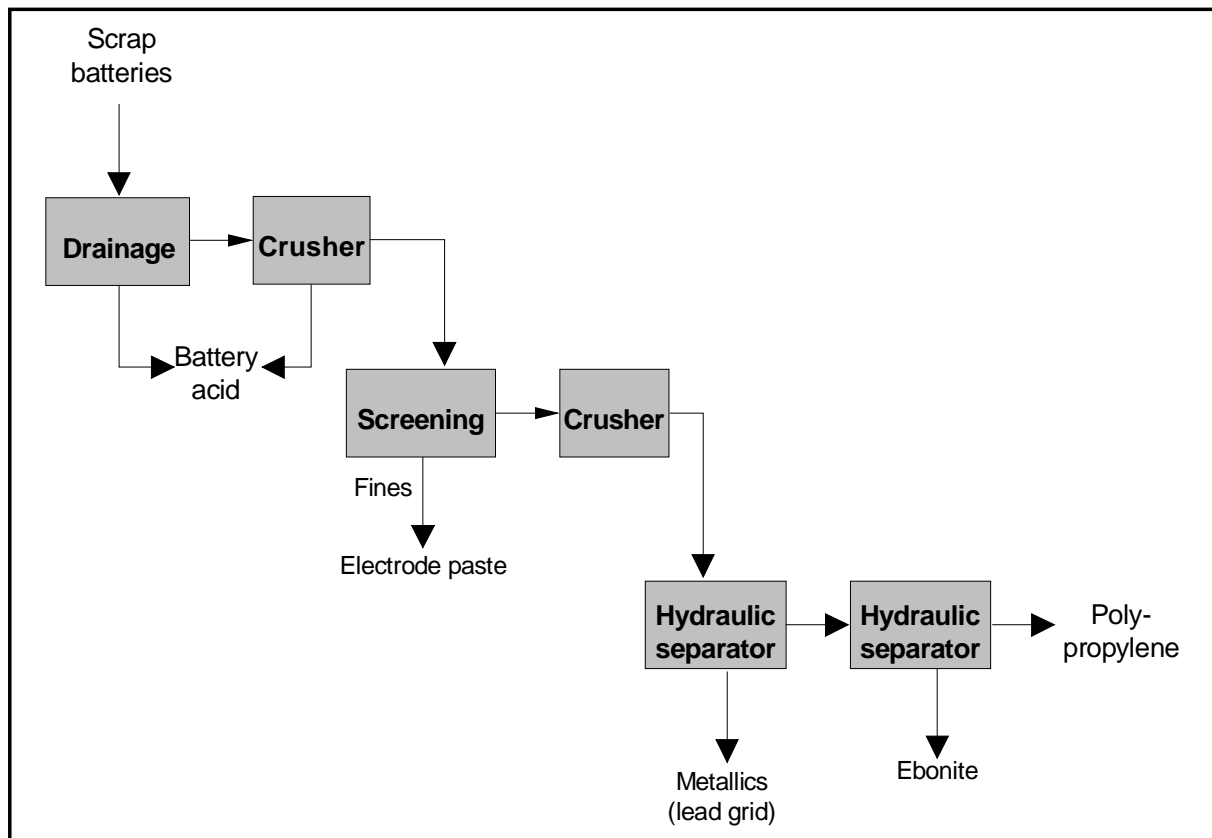
**Table 2-13: Technical processes for lead recycling from lead-acid batteries (examples)**

Basic steps	Name	Reference Plant(s) (examples)	Source
Battery breaking, Separation of different fractions, Desulphurisation of the paste ( $\text{Na}_2\text{CO}_3$ / $\text{NaOH}$ ), Melting of the metallic fraction Smelting of the $\text{PbCO}_3/\text{PbO}$ mixture	Engitec	Muldenhütten Recycling und Umwelttechnik, Freiberg BSB Recycling, Braubach Northfleet (UK)	[68], [114], [29]
Crushing of batteries and drainage, Wet screening, Hydraulic classification, Melting of the metallic fraction	MA process	Harz-Metall GmbH, Goslar	[114]
Crushing of batteries and drainage, Separation of components, Smelting of paste	Penarroya	Metaleurop Escaudoeuvres, Escaudoeuvres (France)	[114]
Crushing of batteries and drainage, Smelting of complete batteries in a shaft furnace	VARTA (Bergsoe)	VARTA Recycling, Krautscheid Landskrona (Sweden)	[114], [82], [91]
Crushing of batteries and drainage, Smelting of complete batteries in a rotary furnace		Metallhütte Hoppecke, Brilon Hetzel Metalle, Nürnberg Metallhütte Schumacher, Rommerskirchen	[74]

#### 2.2.2.4.1 Preparation of battery and scrap materials

For the preparation of scrap lead-acid batteries, there are two basic types of processes in general. Either the batteries are broken up, dismantled and separated into different material fractions like lead, plastic and acid before they are charged in the smelting process (**type 1**) or the entire batteries and cases are processed, after breaking and acid removal (**type 2**).

For **type 1 processes**, on an industrial scale separation technologies such as the MA process and the Engitec process are operated. These processes differ only slightly in the process steps used, but achieve different degrees of separation of the single battery components. A typical scheme of the main steps for battery breaking is shown in Figure 2-7.



**Figure 2-7: Schematic view of the battery breaking steps**

Source: according to Jolly et al. [36]

Hammer mills or shredders are used for crushing the batteries. The battery acid is separated and can either be used for different purposes or is neutralised. In the subsequent screening step, rotating or hydraulic separators are used for the separation of fractions of metallics (e.g. lead grid), electrode paste, polypropylene, ebonite and polyvinyl chloride. The metallic fraction is fed into the smelting furnace separately from the paste. For further treatment of the sulphur containing battery paste, different possibilities to control the sulphur dioxide emissions exist:



- transfer to primary plants for further processing,
- desulphurisation by the addition of sodium hydroxide or sodium carbonate to reduce sulphur dioxide emissions from the subsequent smelting step, and
- charging into the furnace by addition of soda and/or iron.

**Type 2 processes**, like the VARTA process, the Bergsoe process, the Contibat or similar processes, are carried out without initial separation of inputs. After acid drainage the batteries are directly smelted in a furnace. Complete batteries can be smelted in shaft furnaces with the addition of iron or in rotary furnaces with the addition of soda and iron. The preparation of the other inputs comprises the crushing of drosses and oversize scrap and the separation of valuable or deranging substances.

#### 2.2.2.4.2 Smelting furnaces

In secondary lead production plants, different smelting furnaces, mainly short rotary furnaces but also long rotary kilns, reverberatory furnaces, shaft furnaces and the ISA technology, are used for the smelting of scrap materials. The *International Lead and Zinc Association* gives a survey of the Western World's secondary lead smelters in furnace types (c.f. [74]). In total, 169 plants have been in operation (1991). The main plants for processing of lead-acid batteries in Western Europe are shown in Table 2-14.

**Table 2-14: Main plants for processing of lead-acid batteries in Western Europe**

Technology	Number of plants
Smelting of complete batteries in rotary furnaces with addition of soda and iron	≈ 15
Smelting of complete batteries in a shaft furnace with post combustion	4
Separation process with gaining of polypropylene, smelting of undesulphurised paste with soda	≈ 5
Separation process with gaining of polypropylene, external treatment of paste, smelting of metal fraction with silica slag	2
Separation process, paste desulphurisation and smelting	≈ 7

The *shaft furnace* is used for the smelting of drained batteries or battery scrap. The scrap batteries together with other lead containing substances like cable scrap, return slag, filter dusts, fluxes are used as feed materials. For the smelting operation coke is charged in alternate layers. The products of the smelting process are lead bullion containing most of the antimony, sulphur containing lead-iron matte, slag and flue dust. Plastic materials contained in the input are volatilised and finally burnt. *Rotary furnaces* used for the smelting of pre-treated materials are the most common smelting furnaces. Most of these furnaces have a diameter of 3.5 - 4.0 m and a length of 4.0 - 5.0 m. In addition to the size, the respective operation modes differ. Generally, short rotary furnaces are operated batchwise. After the charging of the short rotary

furnace, the input fraction (raw materials, reductants and fluxes) is smelted in the furnace. Heat is supplied by oil or natural gas burners. If sulphur is contained in the input charge, it is removed from the lead and then fixed in the soda slag. At the end of the batch cycle, the produced lead bullion is tapped and transported to the refinery. The slag is tapped in pots or granulated and dumped. The furnace off-gas is led to the gas cleaning devices.

With the *Isasmelt furnace*, paste and metallic grid are processed batchwise in different campaigns. The fuel is injected into the furnace via a lance.

In Germany, only the shaft furnace process and several rotary furnaces are used for the production of lead bullion exclusively from secondary raw materials.

### 2.2.2.5 Lead refining

The final step of lead production is commonly pyrometallurgical (over 90 % world-wide) or less commonly electrolytical refining of the lead bullion. The refining is used to remove a range of impurities from the lead bullion derived from inputs, fluxes and reagents. A typical refining scheme, as exemplary shown in Figure 2-8, can be as follows:

- drossing/decupperising: the pre- and final removal of copper (Colcord process),
- softening: the removal of arsenic, tin and antimony (e.g. using the Harris process or oxygen softening),
- desilvering: the removal of noble metals (Parkes process),
- dezincing: the removal of zinc by vacuum distillation,
- debismuthising: the removal of bismuth (Kroll-Betterton process),
- removal of alkali metals and alkaline-earth metals, and
- finishing by smooth oxidation and addition of sodium hydroxide.

The main processes for the refining of lead bullion are, as a rule, decupperising and the removal of tin, arsenic and antimony, desilvering and dezincing. The processes used in secondary plants for refining are similar to those operated in primary production plants, but the number of operations necessary for secondary lead refining is limited compared to those for primary plants. For example, the removal of copper, silver and bismuth is often not necessary as lead from secondary sources does not contain these substances in quantities [23]. A more detailed description is given in literature, for example by Pawlek [66], Rich [74], Sutherland et al. [83] and Zierock [114].

All the refining processes are carried out in different reactors e.g. kettle furnaces, Harris reactors, reverberatory furnaces, distillation furnaces and induction furnaces. The kettle furnaces are heated by small oil or gas powered burners. The arising intermediate products can be skimmed off from the surface of the molten metal. The kettles are covered with ventilated hoods, which are connected to the gas cleaning system. The off-gases are cleaned in bag



gases and particulates and the disposal of solid wastes. In the following, an overview is given of the main outputs and environmental concerns of the different lead production technologies. To follow the scope of this study, only production processes operated in Germany are considered.

#### 2.2.2.6.1 New direct smelting plants (QSL process, Sirosmelt Process)

Compared to the conventional lead production route, raw material handling, charge preparation, sulphur dioxide conversion, lead bullion refining and by-product treatment has remained nearly unchanged for the new direct smelting process plants applied in Germany [65]. In Table 2-15, the potential sources of controlled and fugitive emissions into the atmosphere from the new direct smelting technologies QSL and Sirosmelt are summarised. For the other new direct lead smelting processes, the drying of the feed and the handling of the dried materials have to be added as sources with a high emission relevance.

**Table 2-15: Potential sources of controlled and fugitive emissions into the atmosphere from new direct smelting plants**

Process unit	Operation/source	Contaminants	f	c
Raw material storage	Handling, storage, transport	Dust	x	x
Smelting reactor	Reactor operation	Dust	x	x
Slag treatment	Slag granulation	Dust, fumes		x
Sulphuric acid plant	Clean gas from acid plant	Gas, mist		x

f: fugitive emissions; c: controlled emissions

Besides the clean gas which leaves the stack behind the sulphuric acid plant, the exhaust gas from the storage and conveying units is the main off-gas flow.

The potential sources of water pollution are summarised in Table 2-16. Liquid effluents can arise from wet off-gas cleaning, slag granulation, cooling water systems, and surface run-off [23]. In general, they are treated in a central waste water treatment plant. Purified water, which cannot be used internally, is discharged.

**Table 2-16: Potential sources of water pollution from new direct smelting plants**

Process unit	Operation/source	Use/treatment options
General	Rain water from roads, yards, roofs	Waste water treatment plant/reuse
	Wet cleaning of roads	Waste water treatment plant
	Cleaning of lorries, ...	Recirculation, waste water treatment plant
Smelting operation	Cooling water from furnace, machinery and equipment	Recirculation
Slag granulation	Wet ESP effluent	Recirculation, waste water treatment plant
	Granulation water	Recirculation
Gas cleaning system	Condensate from gas cooling, wet ESP	Removal of suspended dusts and reuse as feed, waste water treatment plant
	Condensate from mercury removal	After mercury removal to waste water treatment plant
	Leakages	Recirculation
Sulphuric acid plant	Cooling water equipment	Recirculation
	Leakages	Waste water treatment plant
Cadmium plant	Solution after cadmium removal	Waste water treatment plant
	Leakages	Either to cadmium removal or waste water treatment plant
Central waste water treatment plant	Effluent treatment	Internal use, discharge

The main outputs from the new direct smelting plants and their use/treatment options are summarised in Table 2-17.

**Table 2-17: Main outputs from the German new direct smelting plants**

Process unit	Output	Use/treatment options
Smelting reactor	Lead bullion	To refining
Refinery (c.f. Table 2-21)	Lead and lead alloys	Main product for sale
	Doré metals	By-products for sale
	Copper matte/copper dross	For copper production
Slag granulation	Granulated slag	Applicable in certain road construction fields and special concretes
Gas cleaning system	Filter dust	Recycling to lead smelting unit Cadmium and chlorine removal
	Calomel	Saleable by-product
	Waste heat	Power generation or turbines
Sulphuric acid plant	Sulphuric acid	Saleable by-product
Cadmium plant	Cadmium carbonate	Saleable by-product for cadmium production or to be dumped as hazardous waste

Solids which are rich enough in lead (or other metals) are recycled internally. To recover valuable metals, several by-products are processed at the plant site or sold to other companies.

The slag is granulated with a high pressure water jet and can often be used externally, for example in certain applications in road construction. Sulphuric acid produced in the sulphuric acid plant is sold.

#### 2.2.2.6.2 Rotary and shaft furnace process plants using exclusively secondary raw materials

In Table 2-18, the potential sources of controlled and fugitive emissions into the atmosphere from rotary and shaft furnace plants using exclusively secondary raw materials are summarised.

**Table 2-18: Potential sources of controlled and fugitive emissions into the atmosphere from secondary lead production plants**

Process unit	Operation/source	Contaminants	f	c
Raw material storage	Handling, storage, transport	Dust	x	x
Battery treatment	Breaking, separation, drainage	Dust, mist	x	x
Shaft furnace	Gas cleaning	Dust, gases, vapours	x	x
Rotary furnace	Gas cleaning	Dust, gases, vapours	x	x

f: fugitive emissions; c: controlled emissions

In German secondary lead production plants, only surface run-off water is the relevant source for liquid effluents. An overview of the potential sources of water pollution is given in Table 2-19.

**Table 2-19: Potential sources of water pollution from secondary lead production plants**

Process unit	Operation/source	Use/treatment options
General	Rain water from roads, yards, roofs	Waste water treatment plant/reuse
	Wet cleaning of roads	Waste water treatment plant
	Cleaning of lorries, ...	Recirculation, waste water treatment plant
Battery separation	Spills	Used for the desulphurisation/waste water treatment plant
Paste desulphurisation	Spills	Used in the desulphurisation process/waste water treatment plant
Smelting furnace (rotary or shaft furnace)	Cooling water from furnace, machinery and equipment cooling	Recirculation
Waste water treatment plant	Effluent treatment	Reuse for certain applications/discharge

The secondary lead industry is based upon the recovery of lead from secondary sources e.g. scrap, drosses, slags. In general, the outputs and their quantities and compositions vary from plant to plant and depend upon the plant-specific process design and feedstock. The main outputs from German shaft furnace and rotary furnace plants are summarised in Table 2-20.

**Table 2-20: Main outputs from secondary lead production plants**

Process unit (optional)	Output (optional)	Use/treatment options
Acid removal	Sulphuric acid	Acid recovery, neutralisation with lime and processing together with paste
Battery treatment	Battery paste	Processing in primary lead production plants
	Polypropylene	Recycling/compounding
	Ebonite	Waste incineration
	Separators (PVC, glass-fibres)	Waste incineration
	Magnetic fraction	Saleable fraction e.g. for steel production
Paste desulphurisation	Desulphurised paste	Smelting furnace
	Sodium sulphate	By-product for sale
Shaft furnace (incl. gas cleaning)	Lead bullion	To refining/alloying
	Slag	Internal recycling/road construction material
	Iron/lead matte	Processing in primary lead production plants
	Flue dust	Recirculation after removal of chlorine
	Loaded sorbents	Reuse after stripping, burning
Rotary furnace (incl. gas cleaning)	Lead bullion	To refining/alloying
	Soda-slag with soluble heavy metals	Granulation, dumping
	Flue dust	Recycling
	Loaded sorbents	Reuse after stripping, burning
Refining (c.f. Table 2-21)	Refined lead	Main product for sale
Waste water treatment plant	Sludges	Recycling to smelting furnace

During recent years, trends towards carefully breaking of batteries into their components and treating most fractions as potentially valuable by-products have helped to close material cycles and to minimise solid waste deposition. The lead recycling industry has become a net producer of recycled plastic: polypropylene as recyclable material of which the consumption as battery boxes is increasing. For example, since 1988 *Metaleurop S.A.* has been operating a plant for the production of polypropylene (Cookson Penarroya Plastics division). Therefore the polypropylene recycled from lead-acid batteries obtained in *Metaleurop's* secondary smelter plants is used as feedstock [36]. The plant, located in Villefranche sur Saone (France), has two production lines each with a capacity of 40 tons polypropylene per day. The main markets for the recycled polypropylene chips are the automotive industry, horticulture and technical applications. German company L6 operates a compounding plant, which is described in Chapter 3. Residues from battery breaking are hard rubber, PVC and glass fibre separators.

### 2.2.2.6.3 Refining of lead bullion from primary and secondary plants

Depending on the refining steps applied, different outputs and emissions arise from the refining of lead bullion. Emissions of dusts and fumes from the refining operations are captured by hoods connected to a ventilation system. In addition, the removal of drosses and slags can be done with different types of skimming machines to achieve a dust-free operation [114]. For the cleaning of the exhausted gases, different gas cleaning devices can be applied. In Germany, typically dry techniques are applied. The arising by-products are processed internally or externally. Finally, an overview of the main solid outputs from the refining operations and their use and treatment options is given in Table 2-21.

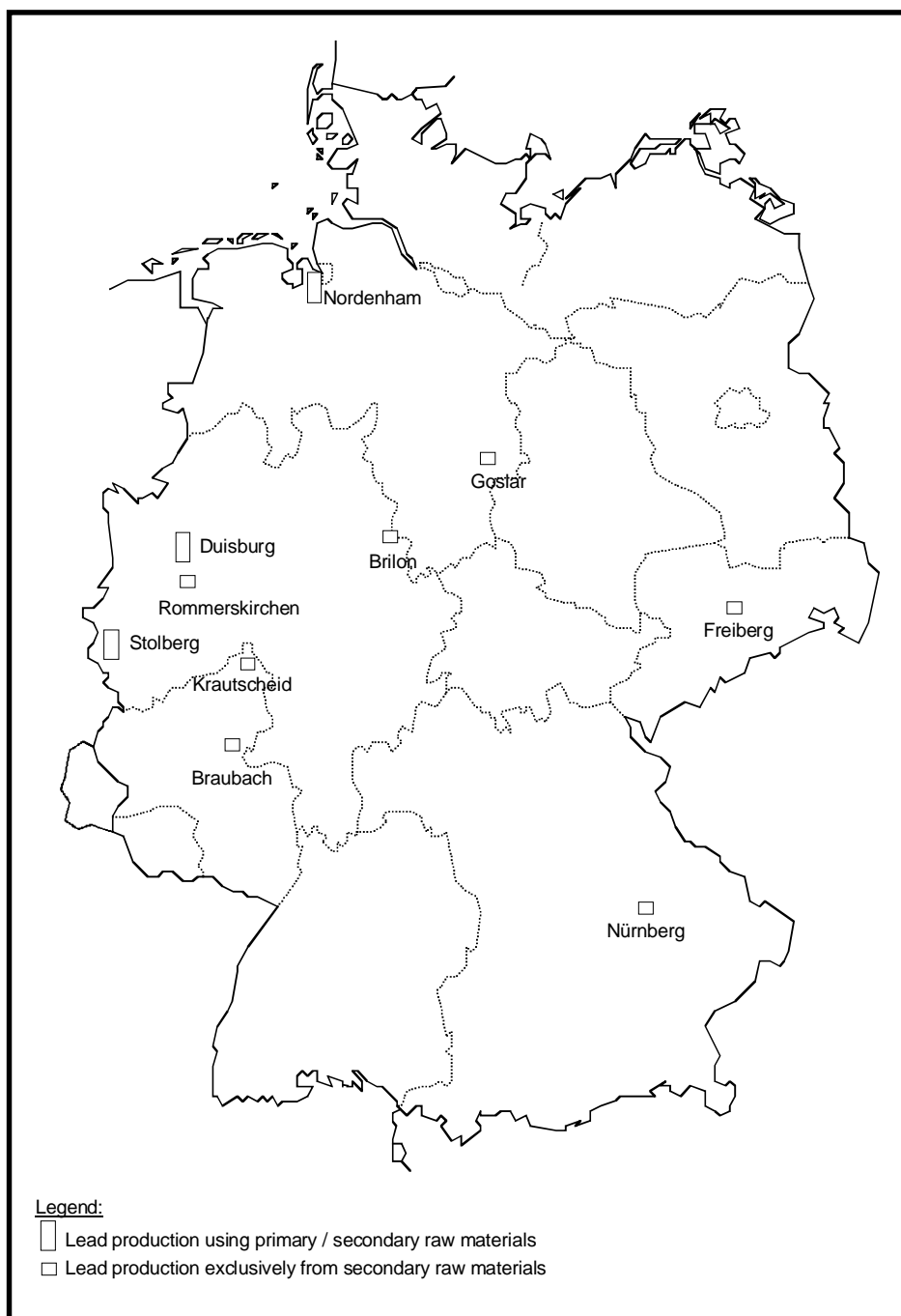
**Table 2-21: Main solid outputs from refining of lead bullion**

Refining step (optional)	Solid output (optional)	Use/treatment options
Drossing/decopperising	Copper dross	Further processing to recover copper and lead
Softening (Harris process/oxygen softening )	Harris slags Antimony slag	Hydrometallurgical treatment for metal recovery Pyrometallurgical treatment for metal recovery
Desilvering	Zinc-silver crust	Recovery of noble metals
Dezincing	Zinc metal	Reuse for desilvering
Debismuthising	Bismuth crust	Recovery of bismuth
Removal of alkali metals and alkaline-earth metals	Mg-Ca oxide dross	Internal recycling as flux
Finishing	Caustic dross	Internal recycling
	Refined lead	Main product for sale

### 2.2.2.7 Lead production plants in Germany

In Germany two plants use bath smelting processes for lead production from primary and secondary materials. In addition, the Imperial Smelting process has to be mentioned because of the relatively large amount of lead produced. However, in the study on hand the IS process is grouped as zinc production process; therefore a detailed description of this process can be found in the sections dealing with zinc production (c.f. Section 2.2.2). Lead production exclusively from secondary material is carried out at several big secondary production plants and some smaller recycling plants. The locations of main German lead production plants are shown in Figure 2-9. Table 2-22 gives detailed information on German plants.





**Figure 2-9: Locations of lead production plants in Germany**

**Table 2-22: Lead production and recycling plants in Germany**

	"Berzelius" Stolberg GmbH	Metaleurop Weser Blei GmbH, Nordenham	Metallhütte M.I.M. Hüttenwerke, Duisburg	Muldenhütten Recycling und Umwelttechnik GmbH, Freiberg	VARTA Recycling GmbH, Krautscheid	BSB Recycling GmbH, Braubach <sup>**) </sup>	Bleihütte Oker, Harz- Metall GmbH, Goslar	Metallhütte Hoppecke GmbH & Co. KG, Brilon	Metallhütten- gesellschaft Schumacher, Rommersk.	Hetzel Metalle GmbH, Nürnberg
<b>Process technology</b>	QSL	Sirosmelt	Imperial Smelting Process	Engitec technology Short rotary furnaces	VARTA process (lead shaft furnace )	Engitec technology Short rotary furnaces	MA technology Short rotary furnace	Short rotary furnace	Short rotary furnace	Short rotary furnace
<b>Special equipment</b>				Waste incineration plant		Compoundation plant				
<b>Feed consump- tion [t/a] / composition</b>	150,000 Lead concentrates: (60%) Lead residues: (40%) (Lead bullion)	130,000 Lead concentrates (45%) Lead residues (55%) (Lead bullion)	250,000 Lead concentrates (50%) Lead/zinc residues (50%)	55,000 Spent batteries Lead residues Scraps	55,000 Spent batteries Lead residues Scraps	55,000 Spent batteries Lead residues Scraps	75,000 Spent batteries, lead residues, scrap	12,000 Spent batteries Lead residues Scraps	18,000 Scraps (75%) Spent batteries (25%)	22,000 Scraps (80%); Spent batteries (20%)
<b>Lead bullion production capacity<sup>*)</sup> [t/a]</b>	90,000	90,000	45,000 <i>100,000 zinc</i>	40,000	35,000	35,000	25,000	10,000	15,000	18,000
<b>Refined lead production capacity [t/a]</b>	150,000	120,000	0	50,000	50,000	40,000	50,000	10,000	15,000	20,000
<b>Main by- products</b>	Sulphuric acid, Slag	Sulphuric acid, Slag	Sulphuric acid, Cadmium carbonate, Slag	Sodium sulphate, PP chips	Slag, Lead-iron matte, Lead dross	PP, Compounded PP chips, Paste	Paste	Slag, Lead dross	Slag, Lead-iron matte, Lead dross	Slag
<b>Certificates</b>	ISO 9002	ISO 9002	-	ISO 9002 ISO 9001 EMAS ISO 14001	ISO 9002	ISO 9001 ISO 9002 EMAS (pilot trial) ISO 14001	ISO 9002	n. a.	ISO 9002	ISO 9002

<sup>\*)</sup> The nominal capacity is mostly larger than the above-mentioned values.

<sup>\*\*)</sup>  BSB stands for the former name **B**lei- und **S**ilberhütte **B**raubach.

### **3 Process technology, abatement techniques and present consumption/emission levels in German zinc and lead production**

#### **3.1 Zinc production in Germany**

In the following, the main zinc production plants operated in Germany are presented in detail. Based on the general descriptions given in Chapter 2, the processes and techniques applied are described. In addition, present consumption and emission levels for each plant are given, where available. Due to the fact, that a strict distinction between primary and secondary process routes is not possible, in this chapter all main German production plants are included.

##### **3.1.1 Hydrometallurgical zinc production plants in Germany**

In Germany, there are two zinc electrolysis plants with an overall production capacity of about 235,000 tons zinc.

###### **3.1.1.1 Zinc electrolysis plant Z1**

###### **3.1.1.1.1 General information**

The Company Z1 operates a zinc electrolysis plant with a capacity of 130,000 t zinc products.<sup>12</sup> 60,000 t/a zinc-aluminium and zinc-aluminium-lead alloys used for continuous galvanising and about 40,000 t/a zinc-aluminium-copper alloys for die casting and similar applications are the main products. The plant comprises the process units, raw materials handling, roasting furnace/sulphuric acid production, leaching plant, purification of solution, electrolysis plant, melting, alloying and casting of zinc products, cadmium plant, and a central water treatment plant. A schematic flowsheet of zinc electrolysis plant Z1 is given in Figure 3-1. The staff consists of about 260 employees in the production related units; about 240 employees work in the maintenance, transport, chemical laboratories, environment, and administration. Some input and output values are given in Table 3-1.

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<sup>12</sup> Process information, presented in this section, mainly base on company information given by company Z1 [58].

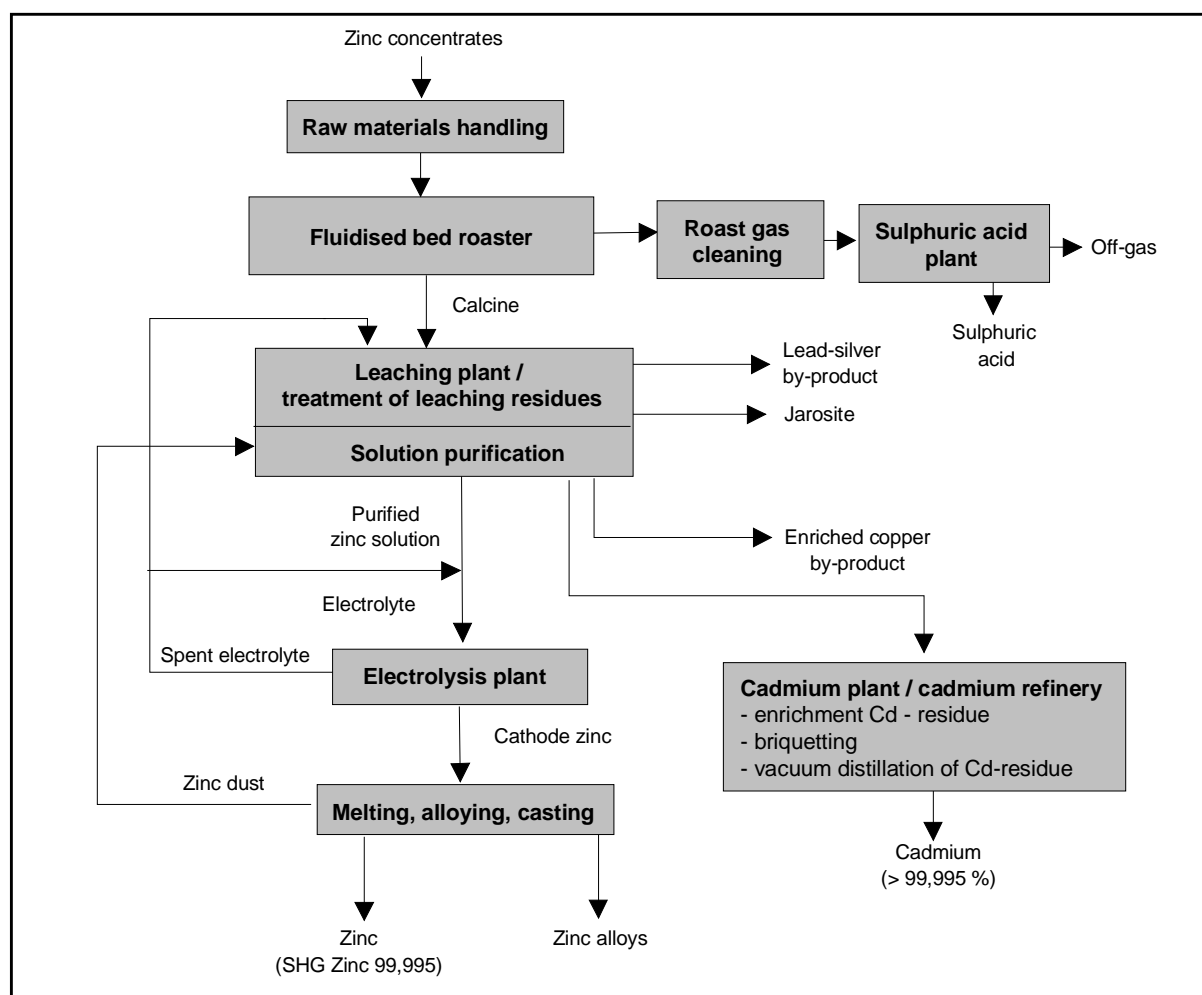


Figure 3-1: Zinc electrolysis plant Z1

Table 3-1: Input and output data for the zinc electrolysis plant Z1

Input	[t/a]	Output	[t/a]
Sulphidic zinc concentrates	225,000	Zinc products	130,000
Electrical energy	n. a.	Lead/silver by-product	15,000
		Sulphuric acid	225,000
		High grade cadmium	400
		Copper by-product	1,000
		Jarosite (dry)	45,000
		Calomel (wet)	6
		Hg-Se sludge (wet)	30

Source: company information company Z1, 1998

### 3.1.1.1.2 Description of the main process units and environmental techniques

In the following, detailed information on main the environmental measures in the different process units are given. Besides technical data, input and output levels are presented, if available.

#### *Raw materials handling*

Sulphidic zinc ore concentrates are the main feed material of the plant. A typical composition is shown in Table 3-2. Other zinc bearing materials like filter dusts, residues, ashes are processed to a minor extent only.

**Table 3-2: Composition of zinc concentrate feed (main elements only)**

Elements	Range [wt.-%]	Average [wt.-%]
Zn	46.7 - 61.9	55.0
Pb	1.0 - 3.2	2.0
Cu	0.03 - 1.03	0.26
Cd	0.14 - 0.48	0.21
Fe	1.6 - 12.0	5.6
S	30.1 - 37.3	31.7
Ag	0.006 - 0.04	0.0125

Source: company information company Z1, 1997

The main sources are Scandinavia, Irish and North American mines. The concentrates are shipped to the company's harbour, unloaded by crane and transported by covered conveyor belts (length 260 m) via a sampling and weighing station to the raw materials storage building with a capacity of up to 60,000 t. The different types of concentrates are stored in separate piles. Mixtures of concentrates are prepared inside the storage building by an overhead crane. The same crane is used to feed the mixed concentrates via covered conveyor belts to the day bin of the roasting furnace.

#### *Fluidised bed roaster/roast gas cleaning/sulphuric acid plant*

The feed mixture is fed to the fluidised bed roaster (grate size 90 m<sup>2</sup>) by two feed belts. At temperatures of about 950°C, metal sulphides are converted into metal oxides and sulphur dioxide by oxygen out of the air blown into the furnace. The produced calcine is cooled, ground in a ball mill and pneumatically transported to two storage bins with a capacity of 5,000 t each, or directly to the intermediate bins of the leaching plant. Off-gases from the ball mill and the transport lines are cleaned in bag filters.

In order to produce high pressure steam, the hot sulphur dioxide containing off-gas is cooled in a waste heat boiler. After dedusting in cyclones and hot electrostatic precipitators it is quenched down in a scrubber. For further purification and the removal of the remaining dust

and volatile compounds (i.e. selenium and mercury compounds) the off-gas is passed through two wet electrostatic precipitators. In the next step, metallic mercury is removed by the Boliden/Norzink process, where saleable Calomel is formed. The cleaned gas is then converted in a double catalysis acid plant into high grade sulphuric acid as a marketable by-product. Multiple tube filters are applied to remove the remaining acid mist before the off-gas is led to the stack (height 125 m).

### ***Leaching plant/treatment of leaching residues***

The leaching plant consists of five leaching steps including the Jarosite process. The calcine is leached in the first step (neutral leaching) consisting of four stirred reactors in series with spent electrolyte at a low acid concentration at temperatures of 90°C. Afterwards the neutral leaching solids and liquids are separated in a thickener. Besides zinc sulphate, the overflow solution contains compounds like copper-, cadmium-, cobalt- and nickel sulphates and has to be further purified. The underflow of the thickener still contains undissolved zinc compounds and is leached in the two following stages at a higher acid concentration and raised temperature. The pulp of the last stage is filtered on two belt filters. The solids contain lead and silver compounds and are sold as a lead-silver concentrate to a lead plant to recover the valuable metals. For the precipitation of dissolved iron from the filtrate, the Jarosite process is used. The iron is precipitated as ammonium jarosite ( $\text{NH}_4[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]$ ) by the addition of ammonia water and calcine to decrease the acid concentration. The ammonium jarosite is separated in thickeners and belt filters with a high efficiency to reduce the content of water soluble compounds (e.g. the content of water soluble cadmium compounds can be reduced to less than 170 ppm). Because of its composition it has to be stored as waste in a specially prepared pond. All reactors and filters of the leaching plant are connected to a central exhaust gas scrubbing system to prevent emissions of aerosols.

### ***Solution purification***

The zinc sulphate solution produced in the leaching plant has to be cleaned of compounds prior to electrolysis to prevent any negative influence to the current efficiency (i.e. due to copper, cobalt, nickel, ...) or co-precipitation with zinc in the cellhouse (i.e. cadmium). For purification, the solution is heated in two hold up tanks (volume: 200 m<sup>3</sup> each) up to 90°C and above and then fed to the first stage. Zinc dust and arsenic trioxide are added to precipitate copper, cobalt, nickel and other elements which are nobler than zinc. The precipitated fraction is separated in filter presses and treated to increase the copper content to approximately 60 %. This enriched copper by-product is sold to copper smelters.

In a second step zinc dust is added to the filtered solution in order to remove the remaining elements like cadmium. The precipitated fraction is separated in filter presses and reprocessed in the hydrometallurgical cadmium plant to produce briquettes with a cadmium content of 98 % and above. The filtered zinc sulphate solution with its high purity is passed as raw

material for the electrolysis process. The exhaust gas from all reactors with the risk of arsine formation is treated in an exhaust gas washing facility with a strong oxidative medium to remove arsine but also other metal compounds. The remaining reactors of the solution purification, the cadmium plant and the copper residue treatment are connected to a scrubber to prevent emission of i.e. metal compounds.

### ***Electrolysis plant (cellhouse)***

The zinc sulphate solution is cooled in cooling towers, mixed with spent electrolyte and fed to the cellhouse at a temperature of about 32°C. Metallic zinc is deposited on the aluminium cathodes and stripped automatically once a day with mechanical stripping machines. The exhaust air from the cooling towers is further purified in a three stage mist collector.

### ***Melting, alloying and casting***

The cathode zinc is melted in an induction furnace and cast with automatic casting machines. Most of the zinc produced is alloyed with aluminium, copper, magnesium or lead to produce zinc alloys for galvanising or die casting purposes. Arising drosses are recycled to the fluidised bed roaster after separation of the metallic fraction. All furnaces are connected to a central bag filter to prevent dust emissions.

### ***Cadmium plant/cadmium refinery***

The cadmium briquettes from the hydrometallurgical cadmium plant are melted. The liquid cadmium is distilled under vacuum to produce high grade cadmium which is cast in ingots. The exhaust gas from the furnaces, the distillation column and the casting section is treated in two electrostatic precipitators in parallel to prevent cadmium emissions.

### ***Central water treatment plant***

All rainwater is collected in a special basin on site and used internally. Contaminated waste water, mainly from the roast gas cleaning unit is treated in a three stage water treatment plant in combination with the waste water from the neighbouring lead plant. Sodium sulphide and sodium hydroxide are used as precipitating agents, iron sulphate as a flocculant in the last stage. The solid residue is partly reused in the lead plant, the remaining part is stored in a public pond for hazardous waste.

### 3.1.1.1.3 Summarised data on outputs and environmental concerns

Table 3-3 shows the main controlled emissions into the air from the zinc electrolysis plant Z1.

**Table 3-3: Controlled emissions into the air from the zinc electrolysis plant Z1 (1994)**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [kg/a]			
		Dust	Zn	Cd	SO <sub>2</sub>
Sulphuric acid plant	59,400	-	-	-	402,762
Transport/grinding of calcine	22,000	86	46.7	0.19	-
Leaching plant	34,600	-	122.1	2.32	-
Solution purification/hydro-metallurgical cadmium plant	31,100	-	49.2	3.44	-
Cooling towers (electrolysis plant)	1,664,300	-	533.2	-	-
Melting, alloying casting (incl. Zinc dust production)	38,100	888.8	550.6	0.06	-
Cadmium refinery	9,200	7.1	1.1	2.72	-

Source: company information company Z1, 1995

The wet cleaning of the roast gas is the only production related source of waste water in the electrolysis plant. Together with the waste water from the neighboured lead production plant, the waste water is treated in one central treatment plant. Data on discharged water from both plants is given in Table 3-4.

**Table 3-4: Waste water from the zinc electrolysis plant Z1**

Process unit	Treatment	Flow [m <sup>3</sup> /h]	Main components [mg/l]		
			Zn	Pb	Cd
Central waste water plant	Discharge	45 - 50	0.01 - 0.2	0.01 - 0.09	0.001 - 0.01

Source: company information company Z1, 1998

Data on arising solid by-products and residues as well as treatment options are summarised in Table 3-5.



**Table 3-5: By-products and residues from the zinc electrolysis plant Z1**

Process unit	By-products/residues	Amount [t/a]	Use/treatment option
Roast gas cleaning	Calomel	6	Sale product
	Mercury-selen residue	30	Dumping
Leaching plant/treatment of leaching residues	Lead-silver concentrate	15,000	Lead production plant
	Jarosite	45,000	Dumping
Solution purification/hydro-metallurgical cadmium plant	Cadmium	400	Sale product
	Copper by-product	1,000	Copper production plant
Waste water treatment plant	Sludges	200	Dumping

Source: company information company Z1, 1998

### 3.1.1.2 Zinc electrolysis plant Z2

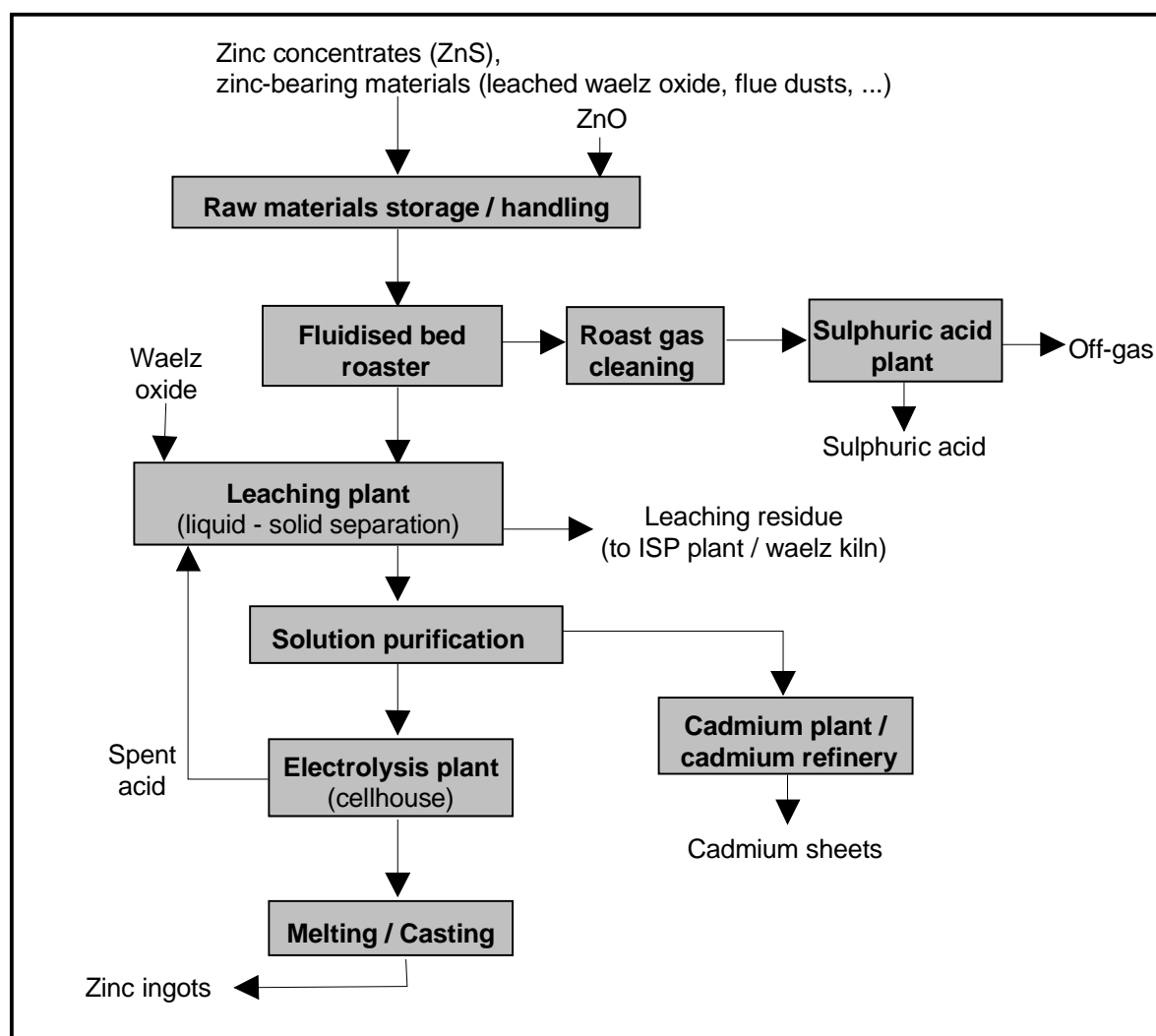
#### 3.1.1.2.1 General information

The company Z2 operates a zinc electrolysis plant with an annual capacity of 105,000 t of electrolytic zinc and comprises the process units: raw materials handling, roasting furnace/sulphuric acid production, leaching plant, purification of solution, cadmium plant, electrolysis plant, melting, and casting of zinc products and a central water treatment plant. Some input and output values are given in Table 3-6. A schematic flowsheet of the zinc electrolysis plant (company Z2) is given in Figure 3-2.

**Table 3-6: Input and output values of the zinc electrolysis plant Z2**

Input	[t/a]	Output	[t/a]
Sulphidic zinc concentrates	170,000	Zinc products	105,000
Zinc bearing materials	40,000	Leaching residue	50,000
Electrical energy	n. a.	Sulphuric acid	160,000
		High grade cadmium	n. a.
		Copper by-products	n. a.

Source: company information company Z2, 1998



**Figure 3-2: Zinc electrolysis plant Z2**

### 3.1.1.2.2 Description of the main process units and environmental techniques

In the following, detailed information on the main environmental measures in the different process units are given. Besides technical data, input and output levels are presented, as far as available.

#### **Raw materials handling**

Sulphidic zinc ore concentrates are the main feed material of the plant. The main sources are mines in Europe and Canada, but also in Middle- and South-America and Australia. The concentrates are shipped to the company's harbour, unloaded by a crane and transported by covered conveyor belts via a sampling and weighing station to the raw materials storage. Beside concentrates, other zinc-bearing materials like ashes, filter dusts and leached waeltz oxide are processed to a smaller degree.

***Fluidised bed roaster/roast gas cleaning/sulphuric acid plant***

The mixture is charged into each of the two fluidised bed roasters (grate size 55 m<sup>2</sup>) via a rotary feed table. At a constant furnace temperature, the conversion of metal sulphides takes place and a roast gas with 12 vol.-% sulphur dioxide is obtained.

**Table 3-7: Chemical composition of calcine (example)**

Component	[wt.-%]	Component	[wt.-%]
Zn	55 - 65	As	0.03 - 0.06
Fe	6 - 9	Tl	0.01 - 0.02
S (SO <sub>4</sub> <sup>2-</sup> )	2 - 3	Bi	0.01 - 0.03
Cd	0.15 - 0.3	Silicic acid	1 - 2.5
Pb	1.5 - 3.0	Lime	0.5 - 2
Cu	0.3 - 1.0	Mg	0.3 - 0.5
Co	0.03 - 0.08	Al <sub>2</sub> O <sub>3</sub>	0.3 - 0.6
Ni	0.03 - 0.08		

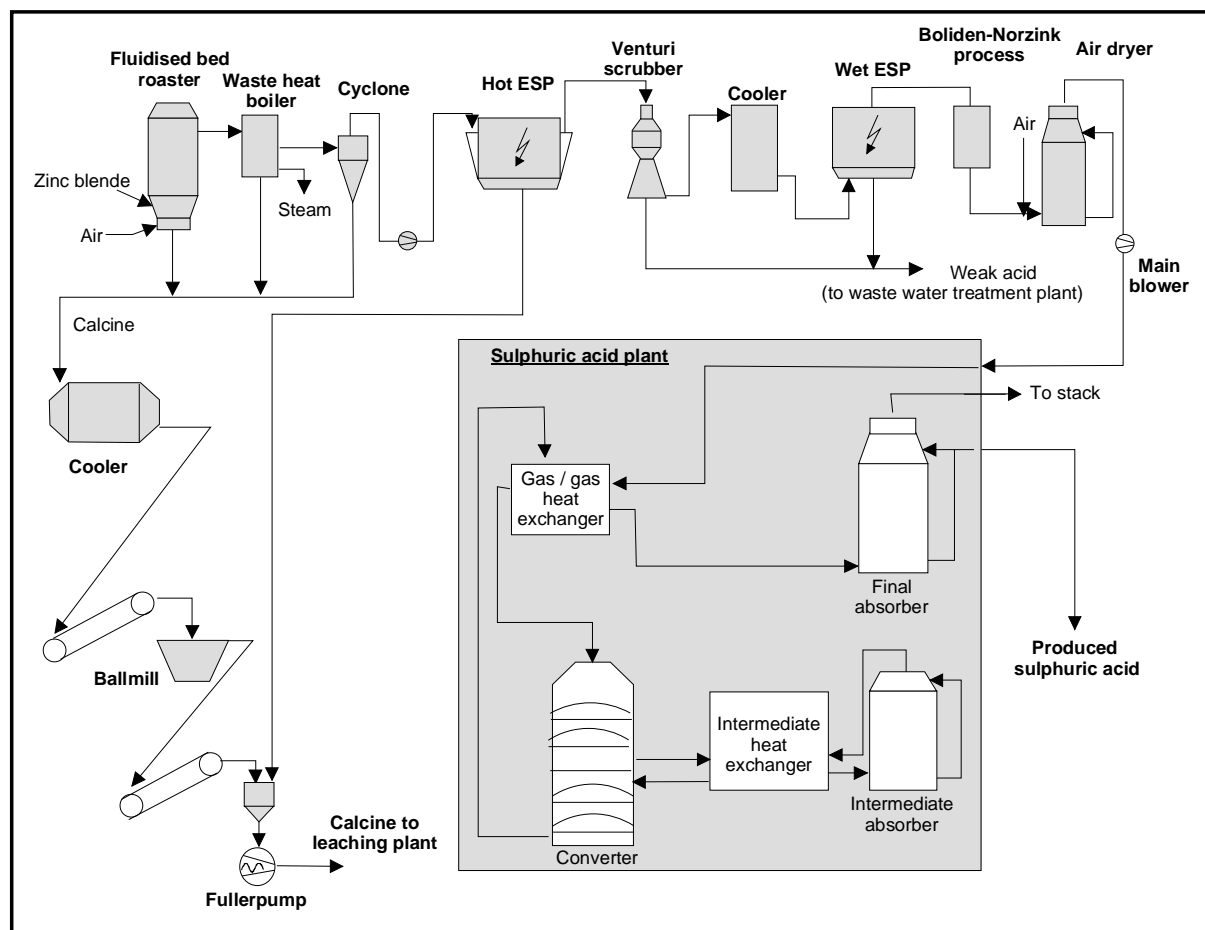
Source: Wiegand [111]

The calcine is precipitated in the different gas treatment units and together with the calcine discharged from the roaster subsequently cooled down to 150°C, ground and pneumatically transported to four storage bins of the leaching plant. A schematic view of the whole roast gas cleaning unit is shown in Figure 3-3.

The heat recovered from calcine cooling in the cooler is used internally. In order to recover the roast gas heat, the hot sulphur oxide containing off-gas is cooled down to 350°C in a waste heat boiler. After pre-dedusting in two hot cyclone groups, it is cleaned in three hot electrostatic precipitators. For further cleaning and cooling, six Venturi scrubbers in parallel and several gas coolers are used. Subsequently the off-gas is cleaned in wet ESPs and the mercury removal plant (Boliden/Norzink process) and then dried in an air dryer. After mercury removal using the Boliden/Norzink process the purified off-gas is passed to the sulphuric acid plant. The acid plant consists of two production lines with a sulphuric acid capacity (96 %) of 700 t/d and 265 t/d respectively. The production of sulphuric acid with a 98 % quality is also possible. As a consequence of a research project, several technical measures have been realised in order to reduce the fugitive dust emissions during the start-up phase of the roaster and during the operation of the calcine preparation and transport equipment<sup>13</sup>. With the installation of a suction ventilation system dust emissions from the calcine coolers, the ballmill, and the start-up phase of the roaster can be collected together with the exhausted ambient air from the roaster shop. The two stage filter system consists of a bag filter followed by a non-dedustable high efficiency sub-micron particulate air filter. A

<sup>13</sup> A detailed description of the project *The reduction of diffuse heavy metal emissions in a roasting plant using process and separation technologies as well as through reduction of uncontrolled thermal air currents* is given by Wiegand [111].

clean gas dust content of less than 1 mg/Nm<sup>3</sup> for the general operation can be achieved. Fugitive dust emissions from the roasters have been reduced by a complete enclosure. To reduce thermal air currents, the chutes of the waste heat boiler are lined with refractory bricks in the dust removal area and also partly insulated.



**Figure 3-3: Roast gas cleaning system of a fluidised bed roaster**

Source: according to Wiegand [111]

Table 3-8 gives some examples of results to show the reduction of total dust emissions achieved by the installation of several reduction measures. The measurements were taken before and after the plant modernisation [111].

**Table 3-8: Reduction of total dust emissions from a fluidised bed roaster**

	<b>Old installation<sup>*)</sup> (1987)</b>	<b>New installation<sup>*)</sup> (1992)</b>
<b>Measures</b>	Fugitive emissions occur during repair operations and by thermal air currents: - no further emission reduction were installed	The following emission reduction measures have been installed: - suction ventilation system - two stage filter system - insulation of waste heat boilers - complete enclosure of the roaster
<b>Total dust emissions [kg/a]</b>	3,350	1,757
<b>Zinc content in dust [kg/a]</b>	1,561	906
<b>Lead content in dust [kg/a]</b>	56	101 (higher value due to a higher lead content in the raw dust)
<b>Cadmium content in dust [kg/a]</b>	9.5	8.2 (high value due to a higher cadmium content in the raw dust)

<sup>\*)</sup> Zinc production capacity: 135,000 t/a

Source: Wiegand [111], Rentz et al. [71]

### ***Leaching plant/treatment of leaching residues***

The calcine is leached in the one-stage leaching plant, the so-called neutral leaching. Mainly zinc, copper and cadmium are dissolved. After the neutral leaching, the solids and liquids are separated in a thickener. The solid residue is de-watered and washed in a filter drum first and then in a filter press and centrifuges. The remaining iron and zinc containing filter cake with a moisture of 17 - 25 % further has to be treated externally. At present the filter cake is processed in a pyrometallurgical IS furnace plant and in waelz kilns.

### ***Solution purification***

The zinc sulphate solution produced in the leaching plant is cleaned in a three stage purification unit. In the first stage the solution is heated up to 90°C, and impurities like copper, nickel, arsenic, etc. are precipitated by the addition of zinc dust and arsenic compounds. The residue is separated with filter presses, washed, filtered again, and stored for sale. The filtered solution is cooled in a heat-exchanger and fed into fluidised bed reactors (Outokumpu process). Zinc dust is added to the filtered solution in order to remove elements like cadmium and thallium by cementation. The cementated fraction is separated by filter presses, mashed and passed to the cadmium plant for further processing. For the final purification again zinc dust is added in the third stage. The purified solution is cooled in cooling towers and passed to the cellhouse.

***Electrolysis plant (cellhouse)***

The cellhouse contains 106 electrolysis cells with 85 anodes and 84 cathodes per cell. The cathode area is 3.5 m<sup>2</sup>. The zinc sulphate solution is mixed with spent electrolyte and fed to the cells. Metallic zinc is formed on the aluminium cathodes and stripped automatically every 24 hours with mechanical stripping machines. Parts of the cell acids are used in the leaching plant. The whole cellhouse is exhausted, the exhaust air is passed to a mist collector.

***Melting and casting***

After drying the cathode zinc is melted in two induction furnaces (total smelting capacity 32 t/h) and tapped in runners. For ingots (1.5 t or 6 t) a special casting machine is used. The off-gases from the furnaces are sucked off at the skimming area and cleaned in bag filters.

***Cadmium plant/cadmium refinery***

The cementated cadmium is leached, precipitated by the addition of zinc dust and concentrated as a sponge. The cadmium sponge is leached. The solution is purified in several steps and a thallium compound can be separated in a filter press. Metallic cadmium is recovered by electrolysis from internal and external residues. The cellhouse contains 15 electrolysis cells with 40 aluminium cathodes and 41 lead anodes each. The electrolysis is operated with a current density between 50 and 100 A/m<sup>2</sup>. The produced cadmium sheets are sold in different shapes e.g. for further processing.

All tanks and vessels are covered. The ventilation system is operated with a slight negative pressure. The exhaust air is cleaned in the central wet scrubber system.

***Central water treatment plant***

All process effluents are treated together with the rainwater in the central waste water treatment plant.

### 3.1.1.2.3 Summarised data on outputs and environmental concerns

Table 3-9 shows the main controlled emissions into the air from the zinc electrolysis plant Z2.

**Table 3-9: Controlled emissions into the air from the electrolysis plant Z2**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [kg/a]			
		Dust	Zn	Cd	SO <sub>2</sub>
Sulphuric acid plant	35,000 - 40,000	-	-	-	250,000 - 300,000
Transport/grinding of calcine	12,000 - 15,000	70 - 90	50 - 60	< 0.2	-
Leaching plant (incl. solution purification and cadmium refinery)	70,000 - 80,000	-	20 - 25	1 - 2	-
Cooling towers (electrolysis plant)	800,000 - 900,000	-	800 - 900	-	-
Melting, alloying and casting	60,000 - 70,000	200 - 240	130 - 170	-	-

Source: company information company Z2, 1998

In Table 3-10 the waste water and process water from the different process units are summarised.

**Table 3-10: Waste water from the zinc electrolysis plant Z2**

Process unit	Treatment	Flow [m <sup>3</sup> /h]	Main components [mg/l]		
			Zn	Pb	Cd
Central water treatment plant	Discharge	30 - 45	0.1 - 0.8	0.1 - 0.3	0.01 - 0.08

Source: company information company Z2, 1998

Data on the solid by-products and residues are shown in Table 3-11.

**Table 3-11: By-products and residues from the zinc electrolysis plant Z2**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Leaching plant	Lead-silver concentrate	n. a.	Lead production plant
	Zinc-iron intermediate	50,000	Zinc production plant
Solution purification	Metallic cementate	n. a.	Copper production plant
Electrolysis plant	Sludge	n. a.	Internal treatment
Central water treatment plant	Gypsum	n. a.	Cement production plant

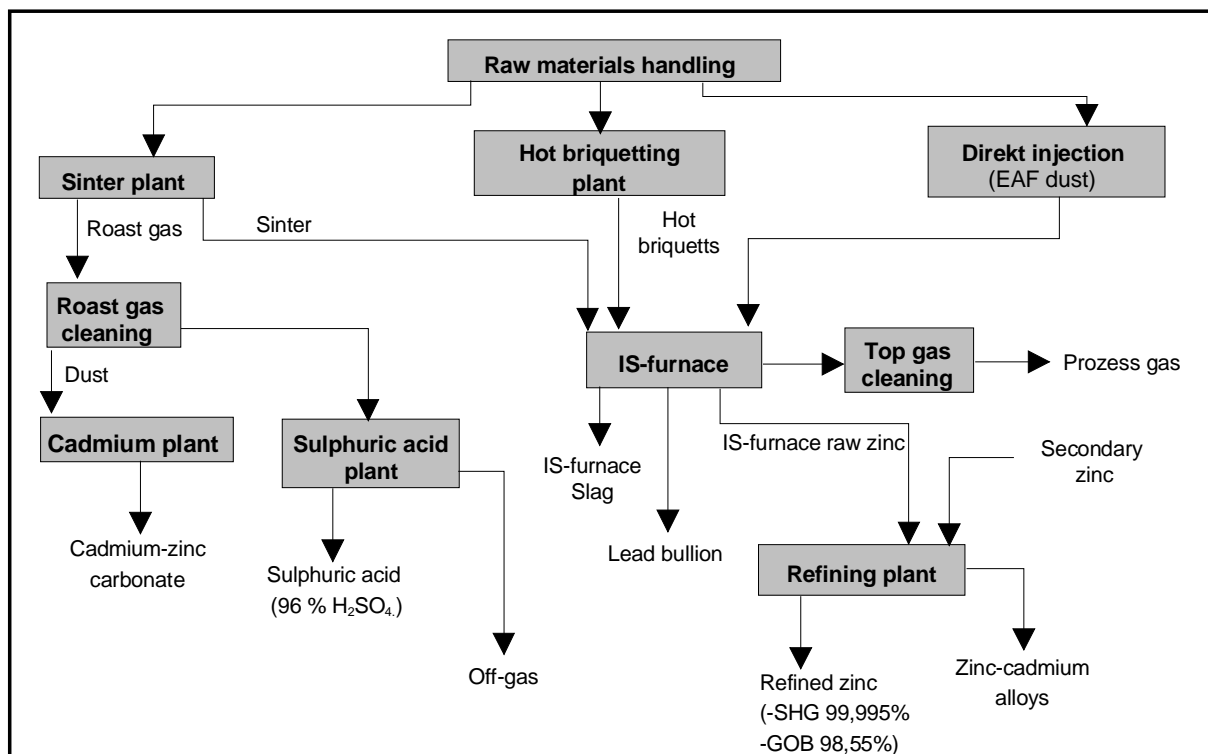
Source: company information company Z2, 1998

### 3.1.2 Pyrometallurgical zinc production in Germany

#### 3.1.2.1 Imperial Smelting Process (ISP) plant Z3

##### 3.1.2.1.1 General information

The company Z3 runs an ISP plant, which comprises the process units: raw materials handling, sinter plant, hot briquetting plant, IS furnace, refining plant, a sulphuric acid plant and a cadmium plant. A schematic view of the plant is given in Figure 3-4.



**Figure 3-4: Imperial Smelting plant by company Z3**

The ISP plant, erected in 1965, produces on average about 100,000 tons of zinc, about 35,000 tons of lead bullion and about 125,000 tons of sulphuric acid per year (1996). Therefore about 250,000 t of input materials are processed (c.f. Table 3-12). At present, the ratio between primary and secondary raw materials is about 1:1.



**Table 3-12: Input and output data of the ISP plant operated by company Z3**

Input	[t/a]	Output	[t/a]
Primary raw materials	125,000	Zinc	100,000
Secondary raw materials	125,000	Lead bullion	35,000
Coke	100,000	Sulphuric acid	125,000
		IS furnace slag	70,000
		Cadmium carbonate	n. a.

Source: company information company Z3, 1998

### 3.1.2.1.2 Description of the main process units and environmental techniques

In the following detailed information on the main environmental measures in the different plant units are given. Besides technical data, input and output levels are presented, if available.

#### *Raw materials handling*

For the raw materials preparation, the common units sinter plant and hot briquetting plant are operated. Recently, company Z3 has put a technology into use, that makes it possible to inject zinc containing dust directly into the furnace, without the need to treat the dust by the waelz-process and hot briquetting. With this process 10,000 tons per year EAF dust are used, at the moment. company Z3 plans to expand the dust injection by 35,000 to 40,000 t/a within the near future. Consequently, in the company Z3 plant three different alternatives exist for raw materials preparation as shown in Figure 3-4 and Table 3-13.

**Table 3-13: Preparation of raw materials for the ISP Plant**

Process unit	Raw materials
Sinter plant	Ore concentrates (Zn, Pb, Cu, Cd, ...) Sulphur containing materials Sludges/residues from water treatment plants Halogen-containing residues
Hot briquetting plant	Ashes and drosses Oxidic raw materials (dry/wet) like waelz oxide, filter dusts Refining residues, ...
Direct injection	Dry and fine materials with zinc, zinc/lead, or lead/copper metal content

Source: Schneider/Schwab [79]

To demonstrate the flexibility of the ISP concerning raw materials, an overview on secondary raw materials processed in the company Z3 plant is given in [79]. The requirements for the chemical composition of the main components can be given only as rough estimates: zinc (15 - 70 %), lead (0 - 70 %), cadmium (0 - 2 %), alkali metals (0 - 10 %), and chlorides (0 - 10 %). In the end, the putting together of the different raw materials is decisive for the

preparation of a suitable input charge. Typical secondary raw materials are shown in Table 3-14.

**Table 3-14: Secondary raw materials for the ISP plant (examples)**

Raw materials Components [wt.-%]	Filter cake cupola	Filter cake cupola	Cupola dust	EAF dust	Lead dust	Zinc-lead oxide	Zinc-iron intermediate
Zn	31	25	31	23	2	44	18
Pb	3	3	0.1	1.3	68	15	7
Cu	0.2	0.1	-	0.1	-	0.4	1.6
C	11	16	5	2	2	0.6	0.2
FeO	10	8	23	35	5	4	33
MnO	2	4	0.6	4	3	0.5	0.5
CaO	2.5	1.5	3	8	3	1.4	2
Al <sub>2</sub> O <sub>3</sub>	2.5	2	2.7	0.7	0.3	0.6	2
SiO <sub>2</sub>	15	13	13	1	-	1	3
Na <sub>2</sub> O	1.8	1	0.6	0.6	0.5	1	0.2
K <sub>2</sub> O	1.0	1.7	0.7	1.0	0.2	2	0.3
Cl	0.4	0.7	0.5	0.6	0.2	4	-
H <sub>2</sub> O	45	26	0.4	10.6	10.4	1.8	30

Source: Schneider/Schwab [79]

### ***Sinter plant***

The sintering belt has a length of 36 m and a width of 2 m. The layer of raw materials is approx. 30 cm thick. A sinter hood is installed to capture off-gases which are led to the roast gas cleaning. At the end of the line the sinter is cooled down, broken and screened. Off-gases from sinter cooling and breaking are dedusted in fabric filters. Sinter fines from screening are recycled to the sinter mixture.

### ***Roast gas cleaning***

The exhaust off-gases from the sinter plant with a temperature of about 300°C are led to a hot ESP. After first dedusting, the off-gases are further cleaned and cooled in wet scrubbers. The Norzink/Boliden mercury removal process is used to reduce the mercury content in the off-gas. For final dedusting, the gas is led in a wet ESP. In the last step the gas is dried with sulphuric acid and fed into the sulphuric acid plant. The sulphur dioxide content is about 5 - 6 vol.-%.

### ***Sulphuric acid plant***

The sulphuric acid plants consists of two double contact plants for the conversion of sulphur dioxide into sulphuric acid.

### ***Cadmium plant***

The cadmium containing dust from the roast gas cleaning is leached with sulphuric acid for cadmium recovery. The lead containing residue is recycled to the sinter plant. Dissolved cadmium is precipitated with soda and separated by filtration as zinc-cadmium carbonate. After thallium separation, the filtrate is passed to the central water treatment station.

### ***Hot briquetting plant***

Finer raw materials (< 10 mm), mainly sulphur free, oxidic materials have to be agglomerated before they are fed into the furnace. Together with fine dusts, these substances are homogenised in a mixer and pelletized on a pelletising disc (diameter: 3 m) by the addition of water. The green pellets produced are heated in a rotary furnace and passed to the roll briquetting press. After briquetting and cooling they can be charged to the IS furnace.

The off-gases from the hot briquetting plant are dedusted in a fabric filter and afterwards cleaned in an activated coke filter to achieve PCDD/PCDF clean gas concentrations of less than 0.1 ng-TE/Nm<sup>3</sup>. The loaded coke is finally injected into the IS furnace through tuyères.

### ***IS Furnace***

The input materials (sinter and briquettes) are charged together with preheated coke in layers through a double bell at the top of the furnace. Preheated air, so-called hot wind with a temperature of about 1,100°C, is blown from below into the shaft furnace using 16 tuyères. For furnace operation the use of up to 45,000 Nm<sup>3</sup>/h is possible. Three cowpers are operated for air preheating. To prevent emissions from charging, the furnace top is equipped with a double bell. Metal containing dust is injected through the tuyères of the furnace to produce metal in the most direct way, this technique is shown in Figure 3-5. Due to the high temperatures on the tuyère level of about 2,000°C, organic compounds like PCDD/PCDF possibly contained in the dust and carbon products, are destroyed.

In order to prevent a re-oxidation of zinc vapour, hot air is injected into the top of the furnace. With partly post combustion of carbon monoxide the temperature at the top of the furnace is kept high. Covered fugitive emissions from the top furnace area are cleaned in a wet ESP. Lead bullion and slag are tapped at the bottom of the furnace and separate by gravity in a forehearth. Lead bullion is sold for further refining to lead refineries. The liquid slag is granulated with high-pressure water and slag granulates with a grain size of about 6 mm are obtained. For *proper* furnace operation, the slag composition has to be *carefully* controlled. A typical composition is shown in Table 3-15.

**Table 3-15: Typical composition of IS furnace slag**

Component	Fe <sub>2</sub> O <sub>3</sub>	Zn	Pb	CaO	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
[wt.-%]	55	7.0	0.7	16.0	18.0	0.9	0.7

Source: company information company Z3, 1998

Eluate values of the granulated IS furnace slag are shown in Table 3-16. After granulation, the IS slag (70,000 tons slag per year) is used for road construction.

**Table 3-16: Eluate values of granulated IS furnace slag**

Criteria	Eluate (according to DEVS4) <sup>*)</sup> [mg/l]
Zn	0.02 - 0.1
Pb	0.005 - 0.1
As	0.001 - 0.02
Fe	0.05 - 0.2
Cu	< 0.001 - 0.05
pH	7 - 11

<sup>\*)</sup> DEVS4: Leaching test according to German DIN 38 414

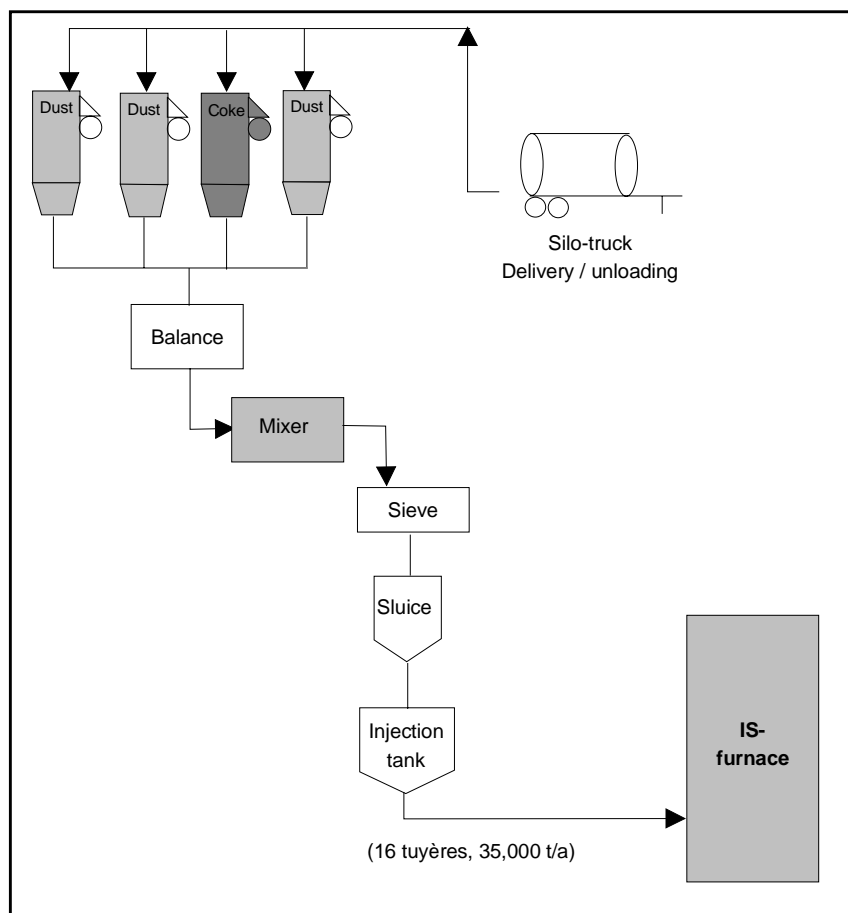
Source: company information company Z3, 1998

### ***Spray condenser and zinc/lead separator***

Zinc is transported with the off-gas at over 1,000°C into the spray condenser, where it is absorbed in a spray of molten lead generated by immersed rotors. Zinc containing condenser lead is pumped from the condenser into the cooling launder, where the liquid zinc is separated by cooling.

### ***IS process gas cleaning***

The raw process gas released through the spray condenser outlet is dedusted in a *desintegrator*. The zinc and lead bearing sludges are recycled to the sinter plant feed. The clean gas values achieved are given in Table 3-17. After cleaning, the process gas is used for coke and wind preheating.



**Figure 3-5: Direct injection of zinc-containing dust**

Source: Schneider/Schwab [79]

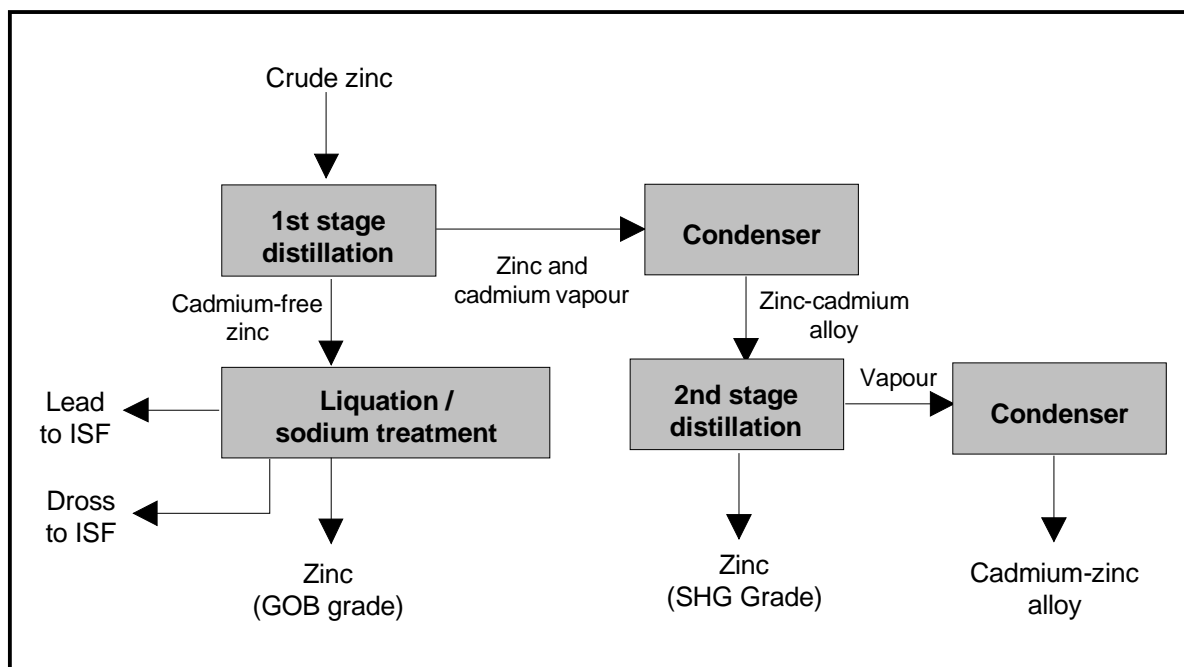
### ***Refining Plant***

Zinc obtained at the IS furnace is sent to a thermal zinc refining process named after the New Jersey Zinc Co. In this process, refining is performed by rectification in indirectly heated refractory distillation columns made of silicon carbide. The whole system consists of 6 distillation columns. Besides shaft furnace raw zinc, other zinc qualities like remelted zinc are processed. For liquation and proportioning, different furnaces are operated in the refining plant. A schematic view of a crude zinc and cadmium refining plant is given in Figure 3-6 [30]. Products of the refining plant are Special High Grade zinc, cadmium free GOB zinc and a cadmium-zinc alloy.

Different techniques for the reduction of heavy metal emissions from the zinc refinery were investigated in a research project carried out between 1985 and 1989<sup>14</sup>. As a result a bag filter was installed for the cleaning of the zinc oxide containing waste gas from the heating

<sup>14</sup> A detailed description of the project *Reduction of heavy metal emissions of a zinc refinery by process- and filter-technologies inclusive energy-removal using a waste heat boiler* is given by Kola/Steil [44].

chambers and the proportioning and liquation furnaces (about 35,000 Nm<sup>3</sup>/h). The dust content in the raw gas (450 mg/Nm<sup>3</sup>) is reduced to less than 5 mg/Nm<sup>3</sup> in the clean gas. Before cleaning, the waste gas with a temperature of about 400°C is cooled in a waste heat boiler and steam is produced.



**Figure 3-6: New Jersey process for the refining of crude zinc and cadmium**

#### ***Water management/waste water treatment***

The ISP plant has a combined waste water system for the treatment of the process water, the cooling water and the surface water. A central waste water treatment plant is operated with two treatment units in parallel, each with a sufficient capacity for the whole waste water flow.

#### ***3.1.2.1.3 Summarised data on outputs and environmental concerns***

Table 3-17 shows the main controlled emissions into the air from the ISP plant. The main emission sources are monitored continuously. In addition, the measurement equipment of five sources has an on-line connection to the local environmental authority for direct access to emission values.<sup>15</sup>

<sup>15</sup> the so-called EFÜ (Emissionsdatenfern-Überwachung)-System

**Table 3-17: Controlled emissions into the air from the ISP plant**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [mg/Nm <sup>3</sup> ]				
		Dust	Zn	Pb	Cd	SO <sub>2</sub>
Charging	90,000	2 - 10	1 - 5	0.5 - 2	0.01 - 0.1	-
Sinter plant	120,000	2 - 20	0.3 - 10	0.1 - 5	0.003 - 0.1	-
Hot briquetting	45,000	< 1	< 1	< 1	< 0.01	-
Sulphuric acid plant	54,000	-	-	-	-	500 - 800
IS furnace	100,000	1 - 5	0.55 - 2.7	0.1 - 0.5	0.001 - 0.005	-
Secondary dedusting (IS furnace/refinery)	200,000	0.4 - 0.6	0.17 - 0.26	0.01	0.001	-
Refining plant	35,000	1 - 5	0.5 - 3	0.05 - 2	0.002 - 0.008	-
Slag treatment	50,000	3 - 18	2 - 10	0.4 - 3	0.008 - 0.02	-

Source: company information company Z3, 1998

In Table 3-18 data on waste water discharged from the ISP plant is summarised.

**Table 3-18: Waste water from the ISP plant**

Process unit	Treatment	Flow [m <sup>3</sup> /h]	Main components [mg/l]			
			Zn	Pb	Cd	As
Central water treatment plant	Discharge	380 - 420	0.05 - 1.0	0.05 - 0.5	0.005 - 0.035	0.005 - 0.1

Source: company information company Z3, 1998

Data on the different by-products and residues are shown in Table 3-19.

**Table 3-19: By-products and residues from the ISP plant**

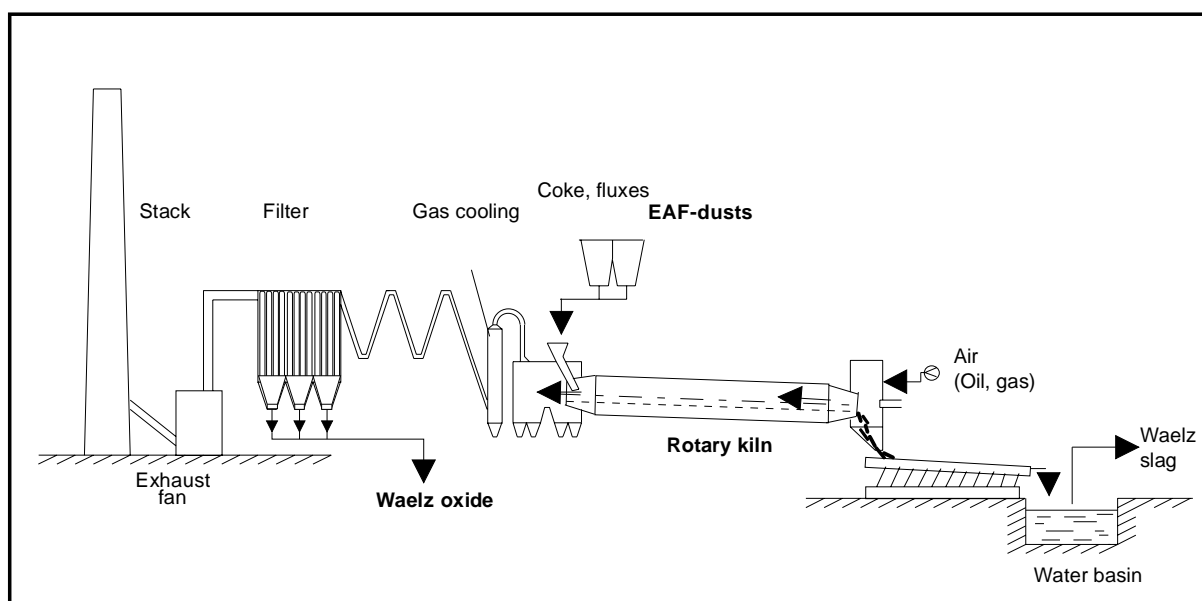
Process unit	By-product/residue	Amount [t/a]	Use/treatment option
IS furnace	Lead bullion	35,000	Sale product (to lead industry for refining)
Sulphuric acid plant	Sulphuric acid	125,000	Sale product
Sinter plant (roast gas cleaning)	Calomel	15	Dumping
	Wet ESP sludge	25	Dumping
Slag treatment	IS furnace slag	70,000	Road construction
	Speiss	85	Dumping
Cadmium plant	Thallium sulphide	25	Dumping

Source: company information company Z3, 1998

### 3.1.2.2 Waelz plants operated in Germany (plants Z4, Z5, Z7)

#### 3.1.2.2.1 General information

Among the high temperature zinc recovery processes, the treatment in a rotary kiln using the waelz technology is the most common in Germany, at the moment. This process, mainly used for the treatment of EAF carbon steel dust but also for retort residues in Germany, recovers zinc as so-called waelz oxide with a share of about 50 - 60 % of zinc and 7 - 13 % of lead. The required percentage of zinc, for example in EAF dust, so that the waelz process is economically viable, is at least 17 - 18 %. Figure 3-7 gives a schematic overview of a waelz plant [73].



**Figure 3-7: Schematic view of a waelz plant**

The waelz oxide produced is sold to zinc smelters and serves as an important resource in the non-ferrous metal industry. The waelz process can be operated with basic or acidic slag treatment. Slag basicity (ratio of  $(\text{CaO} + \text{MgO})/\text{SiO}_2$ ) has to be controlled below 0.5, which means acidic slag or above 2, which means basic slag. To adapt the correct slag basicity, silica or lime-containing materials are mixed with the raw materials.

In Germany, three plants exist for treating EAF dusts, that employ the waelz technology.

#### **Waelz plants Z4 and Z5**

Company Z4 operates a waelz kiln with the acidic slag route, whereas the company Z5 uses the basic slag route. Technical data on the waelz kiln operation at plant z4 and Z5 are summarised in Table 3-20.



**Table 3-20: Technical data on German waelz plants Z4 and Z5**

	Plant Z4	Plant Z5
Treatment capacity for zinc residues [t/a]	60,000	40,000
Total feeding rate <sup>*)</sup> [t/h]	13	9
Production of waelz oxide [t/a]	22,000	13,000
Zinc metal content [t/a]	12,000	9,000
Employment	47	52

<sup>\*)</sup> This value comprises also fluxes and coke.

Source: company information, company Z4/Z5, 1997

Table 3-21 shows input and output data of the waelz plant operated by company Z4.

**Table 3-21: Main input and output data of the waelz plant Z4**

Input			Output		
EAF dust	t/a	60,000	Waelz oxide	t/a	22,000
Coke breeze	t/a	22,000	Slag	t/a	45,000
Sand, fluxes	t/a	14,000			
Electrical energy	MWh/a	6,000			

Source: Hoffmann [31], company information company Z4, 1998

### ***Waelz plant operated by company Z7***

The company Z7 operates a rotary kiln for processing of zinc-bearing materials. This plant uses the acidic slag route with a slag basicity of 0.3 - 0.4. Technical data on the waelz plant are summarised in Table 3-22. A schematic view of this plant is given in Figure 3-8.

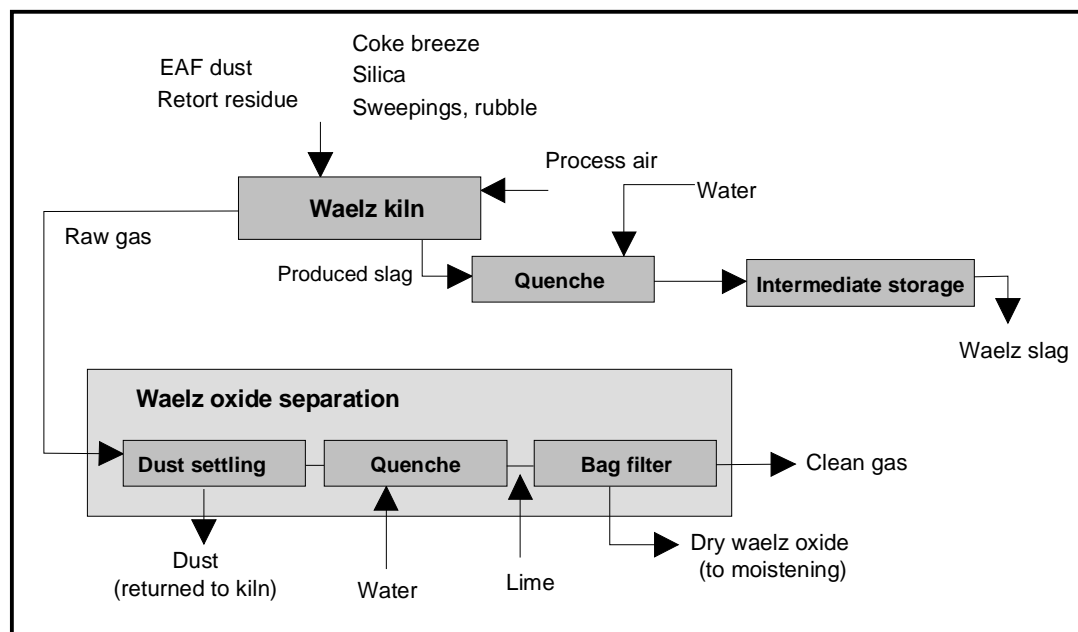
**Table 3-22: Technical data on the waelz plant Z7 (1996/97)**

	Plant Z7
Treatment capacity for zinc residues [t/a]	65,000
Total feeding rate <sup>*)</sup> [t/h]	9
Production of waelz oxide [t/a]	18,000
Zinc metal content [t/a]	9,500
Feeding time [h/a]/operation days [d/a]	7,150/318
Employment	36 <sup>**) </sup>

<sup>\*)</sup> This value comprises also fluxes and coke.

<sup>\*\*)</sup>  At this location, company Z7 operates also a secondary lead production plant. The total employment is 140.

Source: company information, company Z7, 1998



**Figure 3-8: Waelz plant Z7**

Table 3-23 shows the input and output levels of the waelz plant operated by company Z7. A peculiarity of this plant is the usage of retort residues as feed material. The chemical composition of the retort residue processed is given in Table 3-25. In average, the input charge has a zinc content of 16 % and a lead content of 4 %. The waelz oxide is sold for the recovery of lead and zinc. The main customer is a zinc smelting plant owned by company Z1, of which company Z7 is also a 100 % subsidiary.

**Table 3-23: Input and output data of the waelz plant Z7 (1996/97)**

Input	[t/a]	Output	[t/a]
Retort residue, dry	27,700	Waelz oxide	17,000
Zinc carrier, dry (EAF dust, ...)	33,700	Slag	48,200
Coke breeze	10,800	Clean gas [Nm <sup>3</sup> /h]	70,000 - 90,000
Silica	7,500		
Sweepings, rubble	2,100		
Air [Nm <sup>3</sup> /h]	5,000 - 10,000		
Lime	1,000		
Electrical energy [MWh/a]	4,620		
Natural gas [Nm <sup>3</sup> /a]	92,000		

Source: company information company Z7, 1998

### 3.1.2.2.2 Description of the main process units and environmental techniques

In the following, detailed information on the main environmental measures in the different plant units are given. Besides technical data, input and output levels are presented, if available.

#### **Raw materials**

The main feed material for the waelz process are electric arc furnace dusts from the steel production industry with a share of about 80 %. In general, these dusts are already pelletized at the EAF plants and delivered as pellets to the waelz plant. The waelz technology makes it possible to treat a wide range of materials to recycle zinc and other heavy metals. For example, the retort residues with their low zinc content are mixed with EAF dusts to prepare a input mixture with a sufficient zinc content (plant Z7).

The physical aspects of input materials and the conditions for feeding the furnace are not very strict. Nevertheless agglomeration or moisturing is needed. Small amounts of non-pelletized or moistured materials can be accepted. A list of raw materials used in the waelz process is shown in Table 3-24, typical compositions of the main feed materials are given in Table 3-25.

**Table 3-24: Raw materials used in the waelz process**

Raw materials	Comments, Requirements
Electric arc furnace dust	Main input material with a share of about 80 %
New Jersey retort residues	Important input material for one waelz plant, available from an intermediate storage of a neighbouring zinc plant
Other materials: - Cupola furnace dusts, used foundry sands - Zinc sludges, ashes and drosses - Spent shot blastings, catch bullet sands - Sludges from waste water treatment - Used catalysts - Residues from galvanising/chemical industry - Abrasives	

Source: company information company Z4, 1997; company Z7, 1998

**Table 3-25: Typical composition of main feed materials**

	EAf dust (plant 1)	EAf dust (plant 2)	EAf dust (plant 3)	Waelz plant input on average (plant Z4 and Z5)	Retort residue, pure (plant Z7)
Humidity [wt.-%]	15.96	9.47	6.64	n. a.	15 - 30
Zn [wt.-%]	31.78	23.31	19.33	18 - 35	4 - 5.5
Pb [wt.-%]	3.32	2.80	0.84	2 - 7	3.5 - 6
S [wt.-%]	0.48	0.65	0.74	0.5 - 1.5	3 - 4
Cl [wt.-%]	2.88	2.00	0.17	1 - 4	0.04 - 0.07
F [wt.-%]	0.20	0.30	0.44	0.2 - 0.5	0.01 - 0.2
FeO [wt.-%]	25.68	30.62	38.99	20 - 38	9 - 18 (Fe)
MgO [wt.-%]	1.27	1.44	2.84	2.5 - 3	0.4 - 3.8
CaO [wt.-%]	6.91	7.81	11.92	6 - 9	2.5 - 4.5
SiO <sub>2</sub> [wt.-%]	3.56	3.31	2.33	3 - 5	7 - 25
Basicity	2.3	2.80	6.32	1.7 - 4	n. a.
C [wt.-%]	n. a.	n. a.	n. a.	1 - 5	15 - 45
MnO [wt.-%]	n. a.	n. a.	n. a.	4 - 5	0.3 - 1.2 (Mn)
Al <sub>2</sub> O <sub>3</sub> [wt.-%]	n. a.	n. a.	n. a.	0.4 - 0.6	3 - 9
Na <sub>2</sub> O [wt.-%]	n. a.	n. a.	n. a.	1.5 - 2	0.02 - 0.6
K <sub>2</sub> O [wt.-%]	n. a.	n. a.	n. a.	1 - 1.5	0.1 - 0.6

Source: Hoffmann [31], company information company Z7, 1998

### ***Feed storage and preparation***

At the plants Z4/Z5, the raw materials, which are mainly pelletized steel dust, coke breeze and fluxes (silica for the acidic process and CaO-containing materials for the basic process) are delivered by truck, train or ship to the plant and stored separately. For the zinc-containing materials, a feed mixture is prepared in order to ensure a stable and constant input of the main elements like Zn, Fe and alkalines. The materials are fed by shovel loader to a central feeding hopper and transported by covered belt conveyors to the different production bins.

At the waelz plant Z7, the materials are fed via railway wagon and crane to the production bins. At waelz plant Z5, a pelletising plant is installed, in order to permit the acceptance of dry EAF filter dust. The material is blown by pneumatic transport to storage silos. Dry dust, fluxes and fine coke are mixed and water is added. Agglomeration is realised in a mixer and a rolling drum. The pellets consist out of EAF dust, coke and fluxes to favour their reaction in the kiln. With in-house pelletising and directly feeding of fresh pellets into the kiln, the handling by crane and shovel loader can be reduced. Thus the occurrence of fugitive emissions can be minimised.

The non-pelletised charge is reclaimed through weighing feeders and carried by belt conveyors to the feeding pipe of the kiln. The quantity of reduction material, according to the zinc content and fluxes for the slag quality can be controlled by the different weighing

equipment. For example, for acidic slag operation, a basicity of less than 0.5 can be achieved by the addition of sand.

### **Rotary kiln**

In the kiln the solid materials are first dried and heated up by the hot gas passing counter-currently through the kiln. At a temperature above 1,100°C metal oxides are reduced and the zinc and lead are evaporated into the gas atmosphere. These metal vapours from the charge are oxidised in the gas atmosphere, which is operated with a surplus of air to obtain the zinc and lead oxide and subsequently passed with the off-gases to the gas cleaning system. Waste gases from the furnace mouth are covered with a primary hood and cleaned in a bag filter (c.f. Table 3-26).

### **Gas cleaning system**

The mixed oxide is drawn from the kiln with the flue gases for separation in the gas cleaning system. The off-gas temperature is between 650 - 750°C. In a first step the coarse particles, mainly as mechanical carry over from not pelletized steel dust, are settled in a dust chamber. This fraction is directly recycled to the input charge. The hot process gases are cooled down in the following step. Used devices can be evaporation coolers, pipe coolers, pocket coolers or other coolers with direct or indirect cooling. The first part of the product is reclaimed in the gas cooling step but most of the waelz oxide is filtered from the off-gas in bag house filters or ESP. The clean gas has a dust content of less than 10 mg/Nm<sup>3</sup> (c.f. Table 3-26). The cleaned off-gases are exhausted through a stack by a fan used to control draft conditions in the overall system.

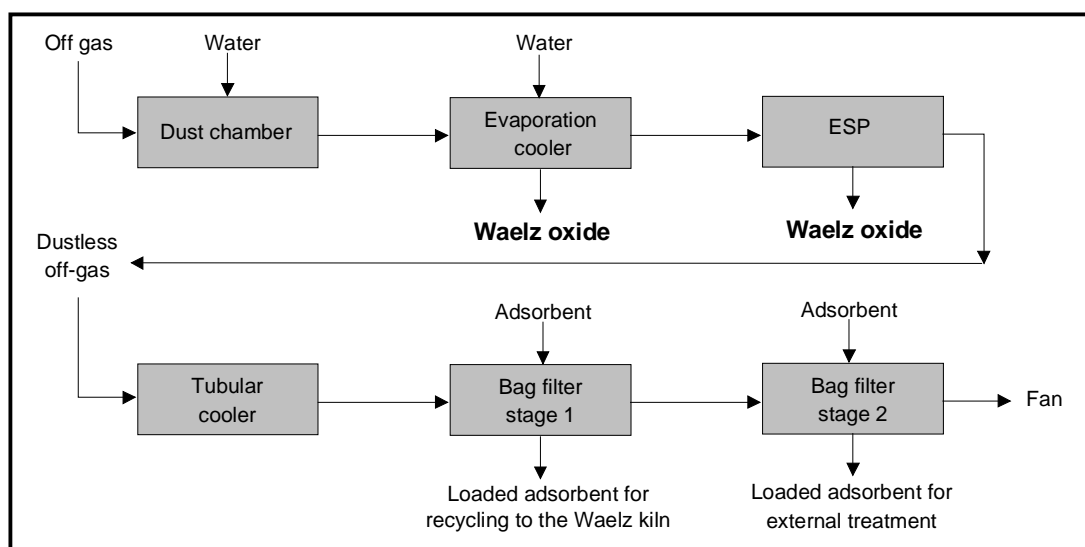
**Table 3-26: Effects of different gas cleaning devices on clean gas composition (Examples, plant Z4)**

Off-gas source	Rotary kiln			Rotary kiln mouth
Gas cleaning device	Dust chamber, evaporation tower, ESP (until 3/94)	Dust chamber, pipe cooler, bag filter (until 11/96)	Dust chamber, evaporation tower, ESP, pipe cooler, filtration, bag filter (actual)	Hood, bag filter
Off-gas stream [Nm <sup>3</sup> /h]	52,000	42,000	38,000	7,500
Dust [mg/Nm <sup>3</sup> ]	12	5	2.8	5.2
Zinc [mg/Nm <sup>3</sup> ]	0.4	0.26	0.1	2.64
Lead [mg/Nm <sup>3</sup> ]	0.9	< 0.1	< 0.1	0.55
Cadmium [mg/Nm <sup>3</sup> ]	0.02	< 0.01	< 0.001	< 0.001

Source: company information company Z4, 1998

Since 1997 at one waelz plant (plant Z4), the conventional gas cleaning system has been supplemented in order to reduce mercury and dioxin emissions. Therefore two additional cleaning steps (bag filters with adsorbent injection) have been installed after the electrostatic precipitator, as shown in Figure 3-9. The nearly dustless off-gas leaves the ESP at a

temperature of about 330°C. A tubular cooler is used for further cooling down to 120°C to reach the entrance temperature of the two downstream bag filters. The injection of a three-component adsorbent, a mixture of activated lignite coke dust, lime hydrate and limestone, allows the adsorption of dioxin and mercury components. The loaded adsorbent is separated by filtration in both bag filters and recycled to the rotary kiln (bag filter 1) or treated externally (bag filter 2). Using this combination of adsorption and filtration (so-called *filtrorsorption*) PCDD/PCDF clean gas values of less than 1 ng-TE/Nm<sup>3</sup> can be achieved [31].



**Figure 3-9: Gas cleaning system of the waelz plant Z4**

### *Slag treatment*

The produced slag is discharged continuously from the kiln end and cooled in a water pond. Depending on the technology used (treatment of acidic or basic slag) the slag is screened, crushed and passed to a magnetic separator to recover free coke breeze, which is recycled into the furnace. At one plant (plant Z7), the coke content in the slag is rather low, because of the plant specific operation practice. Therefore a coke recovery is not necessary at this plant.

The waelz slag is not a liquid (or molten) slag. In the case of the basic process, the slag is dry; however the acidic slag is a pasty semi-molten slag. The heavy metal content is very low and there are few water-soluble components. An example of the composition of acidic waelz slag can be found in Table 3-29. Eluate values of acidic waelz slag, which are lower than the values of basic slag, are shown in Table 3-27.

**Table 3-27: Eluate values of acidic waelz slag (Examples, plant Z4)**

Criteria	Eluate (according to DEVS4) <sup>16</sup>		
	Waelz slag [mg/l]	TVo <sup>16</sup> [mg/l]	Z1.1 <sup>16</sup> [mg/l]
Zn	0.05	5	0.1
Pb	0.02	0.04	0.04
As	0.008	0.01	0.01
Cr <sub>tot</sub>	0.002	0.05	0.03
Ni	0.005	0.05	0.05
Fe	0.5	0.2	-
Cu	0.05	3.0	0.05
F	1	1.5	-
Cl	5	250	10
pH	9.9	6.5 - 9.5	6.5 - 9.5

Source: Hoffmann [31]

Due to the favourable lixiviation, acidic and basic slag are used as road construction material for sub-surfaces and underground preparation. During the cooling of waelz kiln slag, a dust and steam containing ventilation gas arises (c.f. Table 3-28).

**Table 3-28: Raw and clean gas values from slag treatment (plant Z4)**

Off-gas source	Slag treatment	
Gas cleaning device	Hood, wet scrubber with two ionisation fields	
Off-gas stream [Nm <sup>3</sup> /h]	20,000 - 25,000	
	Raw gas	Clean gas
Dust [mg/Nm <sup>3</sup> ]	5 - 20	2 - 5
Zinc [mg/Nm <sup>3</sup> ]	1 - 3	0.5 - 1
Lead [mg/Nm <sup>3</sup> ]	2 - 5	0.5 - 1
Cadmium [mg/Nm <sup>3</sup> ]	0.002	< 0.001

Source: Kola et al. [42], company information company Z4, 1998

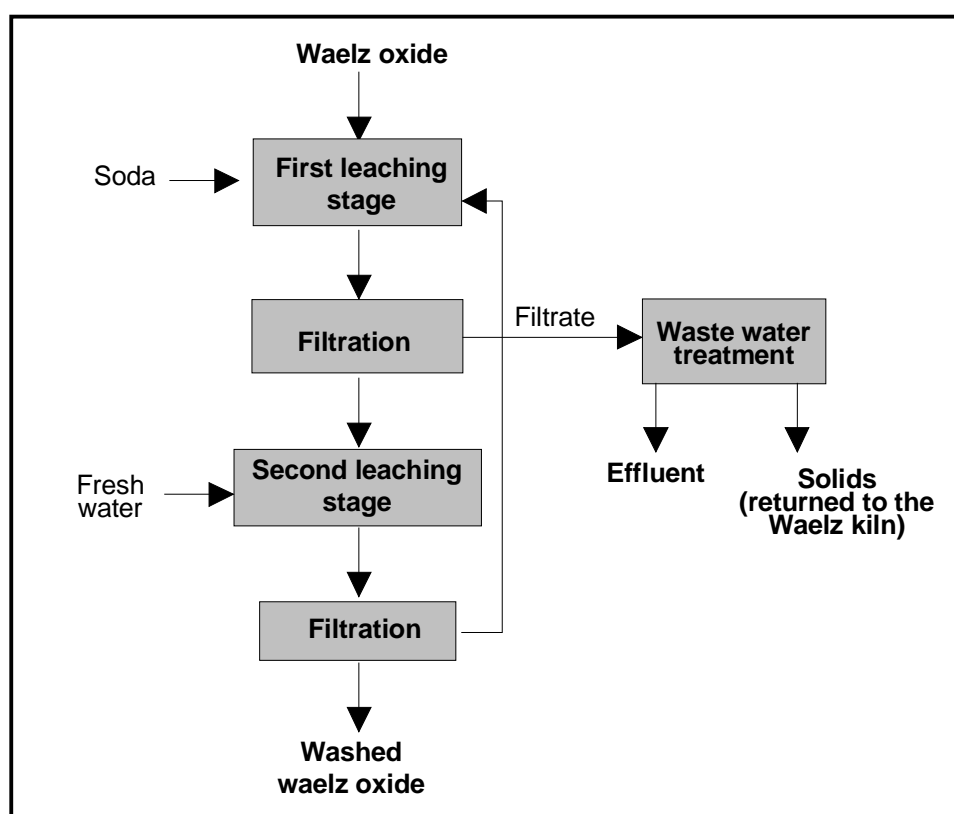
The content of solids is approx. 5 - 20 mg/Nm<sup>3</sup> with a lead content of about 2 - 5 mg/Nm<sup>3</sup>, a zinc content of 1 - 3 mg/Nm<sup>3</sup>, and a cadmium content of 0.002 - 0.005 mg/Nm<sup>3</sup>. These gases are normally captured in a hood and dedusted using wet or dry gas cleaning devices. At waelz plant Z7, the raw gas is dedusted with two bag filters; depending on the process conditions clean gas values of 3 - 6 mg/Nm<sup>3</sup> are achieved. The off-gas volume amounts to 15,000 - 25,000 Nm<sup>3</sup>/h. Concerning wet gas cleaning devices, scrubbers cannot reach sufficient

<sup>16</sup> **DEVS4**: Leaching test according to German DIN 38 414 ; **TVo**: Limit value for eluate according to German regulations concerning drinking water; **Z1.1**: (Regional) limit value for eluate from mineral material valid for North-Rhine Westphalia (c.f. [31]).

separation efficiencies due to the small particle size in the ventilation gas. On the other hand, the installation of a suitable wet ESP requires a very high investment. As an alternative, a combination of a scrubber with two ionisation fields is installed at one plant (plant Z4).<sup>17</sup> It has been shown, that the collection efficiency of this scrubber is as high as for a conventional wet ESP. At the same time the investment as well as the operating costs have been considerably lower [42]. An alternative to the wet scrubber with ionisation fields is the injection of the vapours coming from the slag cooling back to the main off-gas stream. At the waelz plant Z5, the vapours are sucked off by a ventilator and injected into the kiln' off-gas duct between the dust chamber and the cooler.

### ***Waelz oxide leaching***

At plant Z5, waelz oxide is leached in a two step counterflow washing plant in order to remove chlorides and fluorides, which are critical elements for the hydrometallurgical route of zinc production (c.f. Figure 3-10).



**Figure 3-10: Waelz oxide leaching (plant Z5)**

Waelz oxide and filtrate from the second step are mixed and soda is added in order to remove chlorides by carbonates. At a temperature of 50°C and a pH of 11 nearly 95 % of the chlorides and 50 % of the fluorides are dissolved and lead-carbonates are formed. After a solid-liquid

<sup>17</sup> The installation and the usage of the ionisation scrubber is described in detail by Kola et al. [42].



separation, the solids are mashed with fresh water to remove the remaining alkalines from the waelz oxide. In a final solid-liquid separation, the moisture content of the washed waelz oxide is reduced to 18 %. The filtrate from the second step (washing) is used for the first step (leaching) in the waelz oxide processing. Fresh water is only used for the second step. The filtrate from the first step is sent to a waste water treatment plant. Before heavy metals are precipitated flourine is removed as well. The solids from the waste water treatment plant are recycled to the waelz kiln. The produced waelz oxide is a filter cake with a low chloride and fluoride content of less than 0.1 % and can be sold to electrolytic zinc smelters, where it is well-suited due to its low iron and sulphur content. The chemical analysis of washed and unwashed waelz oxide is shown in Table 3-29.

**Table 3-29: Chemical analysis of different output fractions from waelz plants (examples)**

Component	Acidic waelz slag (plant Z4)	Waelz oxide unwashed (plant Z5)	Waelz oxide washed (plant Z5)	Waelz oxide unwashed (plant Z7)	Waelz slag (plant Z7)
Zn	0.5 - 3	55 - 58	60 - 68	48 - 55	1 - 3.5
Pb	0.2 - 1.0	7 - 10	9 - 11	8 - 13	0.5 - 2
S	1.5 - 2.5	0.5 - 1	0.5 - 1	1.6 - 2.0	1 - 3
F	0.1 - 0.25	0.4 - 0.7	0.08 - 0.15	0.15 - 0.25	0.15 - 0.25
Cl	0.003 - 0.05	4 - 8	0.05 - 0.1	4 - 7	0.01 - 0.05
C	3 - 8	0.5 - 1	1 - 1.5	1 - 2	1.5 - 5
FeO	30 - 40	3 - 5	4 - 7	2 - 4 (Fe)	20 - 35 (Fe)
MnO	5 - 6	0.1 - 0.5	0.1 - 0.5	0.2 - 0.4 (Mn)	1 - 2 (Mn)
CaO	8 - 9	0.6 - 0.8	0.7 - 1.2	0.5 - 1 <sup>1)</sup>	6 - 9
MgO	3 - 4	0.4 - 0.5	0.4 - 0.5	0.3 - 0.5	3 - 4
Al <sub>2</sub> O <sub>3</sub>	2.5 - 3.5	0.1 - 0.15	0.1 - 0.2	0.3 - 0.5	5 - 8
SiO <sub>2</sub>	35 - 37	0.5 - 0.7	0.5 - 1	0.5 - 1	25 - 35
Na <sub>2</sub> O	1.2 - 1.6	2 - 2.5	0.1 - 0.2	0.5 - 1.5	0.5 - 1.5
K <sub>2</sub> O	0.7 - 0.9	1.5 - 2	0.1 - 0.2	1 - 2	0.5 - 1
As	0.02	n. a.	n. a.	n. a.	n. a.
Cr <sub>tot</sub>	0.07	n. a.	n. a.	n. a.	n. a.
Ni	0.30	n. a.	n. a.	n. a.	n. a.
Cu	0.21	n. a.	n. a.	n. a.	n. a.

<sup>1)</sup> An injection of CaO into the raw gas is possible.

Source: Hoffmann [31], company information company Z7, 1998

### **Water management/waste water treatment**

The waelz plant can be operated effluent-free as the cooling water for slag cooling is recirculated [42]. Evaporation losses due to slag cooling are replaced e.g. by captured precipitation water or machinery cooling water. Waste water from the waelz oxide leaching, if applied, are treated in the waste water plant.

### 3.1.2.2.3 Summarised data on outputs and environmental concerns

Table 3-30, Table 3-31 and Table 3-32 show the main controlled emissions into the air from the waelz plant.

**Table 3-30: Controlled emissions into the air from waelz plant Z4**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [mg/Nm <sup>3</sup> ]			
		Dust	Zn	Pb	Cd
Off-gas rotary kiln	30,000 - 40,000	1 - 5	0.1 - 1	< 0.1	< 0.001
Gases from the kiln mouth	5,000 - 10,000	2 - 5	1 - 3	0.5 - 1	< 0.001
Slag cooling	20,000 - 25,000	2 - 5	0.5 - 1	0.5 - 1	< 0.001

Source: company information company Z4, 1998

**Table 3-31: Controlled emissions into the air from waelz plant Z5**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [mg/Nm <sup>3</sup> ]			
		Dust	Zn	Pb	Cd
Off-gas rotary kiln	60,000	2 - 3	1 - 2	0.1 - 0.3	< 0.01
Gases from the kiln mouth	10,000	1 - 2	0.5 - 1	< 0.5 - 1	< 0.01

Source: company information company Z5, 1998

**Table 3-32: Controlled emissions into the air from waelz plant Z7**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [mg/Nm <sup>3</sup> ]				
		Dust	Zn <sup>*)</sup>	Pb <sup>*)</sup>	Cd <sup>*)</sup>	SO <sub>2</sub>
Off-gas rotary kiln	70,000 - 90,000	3 - 5	45 - 55	10 - 13	0.05 - 0.1	60 - 100
Gases from the kiln mouth	15,000 - 25,000	3 - 6	40 - 50	10 - 20	0.005 - 0.01	-

<sup>\*)</sup> The content of the component in the dust [wt.-%].

Source: company information company Z7, 1998

Purified water from the central water treatment plant is discharged. Exemplary data are shown in Table 3-33.

**Table 3-33: Data on waste water from waelz plant Z5**

Process unit	Amount [m <sup>3</sup> /a]	Flow [m <sup>3</sup> /h]	Main components [mg/l]		
			Zn	Pb	Cd
Central water treatment plant	50,000 - 60,000	9 - 10	0.8 - 1.0	0.3 - 0.5	0.05 - 0.2

Source: company information company Z5, 1998

Data on solid by-products and residues from waelz plants are shown in Table 3-34, Table 3-35 and Table 3-36.

**Table 3-34: By-products and residues from waelz plant Z4**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Slag treatment	Waelz slag	45,000	Road construction
Rotary kiln	Refractory materials	150	External recycling
Gas cleaning	Loaded adsorbent	60	Dumping

Source: company information company Z4, 1998

**Table 3-35: By-products and residues from waelz plant Z5**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Slag treatment	Waelz slag	39,000	Road construction, drainage layer for landfills
Rotary kiln	Refractory materials	100	External recycling

Source: company information company Z5, 1998

**Table 3-36: By-products and residues from waelz plant Z7**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Slag treatment	Waelz slag	45,000 - 50,000	Dump rehabilitation
Rotary kiln	Refractories	250 - 300	Crushing and recycling to kiln

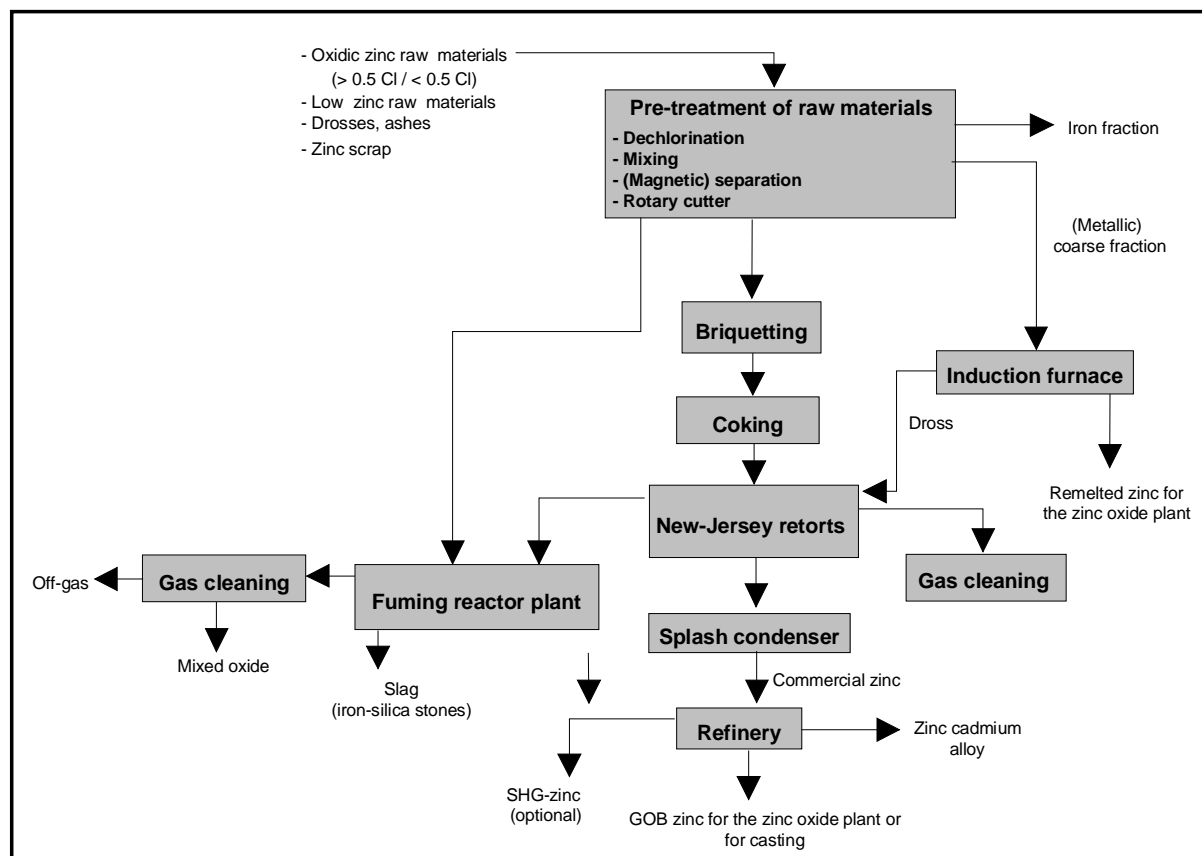
Source: company information company Z7, 1998

### 3.1.2.3 New-Jersey retort plant Z6

#### 3.1.2.3.1 General information

The company Z6 is running the New-Jersey retort process. About 20,000 t/a high grade zinc and 6,500 t/a of remelted zinc are produced from various secondary raw materials. A schematic view of the whole plant is given in Figure 3-11. Since the end of 1996, a new fuming reactor plant for secondary raw materials with a low zinc content is in operation. This plant uses a smelting cyclone technology developed by KHD Humboldt Wedag [70]. The whole plant is certified according to ISO 9002.

The plant comprises the process units: pre-treatment of raw materials, coking furnace, New-Jersey retorts, New Jersey rectification, fuming reactor plant, the induction furnace, and the zinc oxide plant.



**Figure 3-11: Secondary zinc production using the New Jersey retorts (company Z6)**

### 3.1.2.3.2 Description of the main process units and environmental techniques

In the following, detailed information on the main environmental measures in the different plant units are given. Besides technical data, input and output levels are presented, if available.

#### *Pre-treatment of raw materials*

The feed materials are flue dusts from cupola furnace plants and steel plants, slurries from the off-gas cleaning of blast furnaces, galvanising plants, zinc ashes and drosses, spent pot lining and metallic shredder fraction. The typical raw materials and their origin are shown in Table 3-37. Mixed raw materials containing oxides and metals have to be separated into oxide and metallic fractions. Oxidic raw materials with a high content of zinc chloride are leached with water and soda in order to reduce the chlorine content below 0.5 %. Otherwise the operation of the zinc condenser could cause technical problems. The impure salt solution obtained is evaporated and then has to be deposited. Oxidic raw materials are ground and dried to the optimal grain size and humidity, mixed with coking coal, sulphite liquor as binder and briquetted. The briquettes are autogeneously coked and fed to the *New Jersey retort* with a temperature of 850°C. Metallic raw materials with a particle size lower than 400 mm are fed directly to the *New Jersey retort*. Zinc scrap is cut in a rotary cutter into small pieces. In a magnetic separation iron parts are separated for external treatment.

**Table 3-37: Feed materials for the New Jersey retorts process route and their origin**

Feed materials	Origin
Flue dusts	Cupola furnaces (processing of zinc containing fractions) Fusing plants Steel works Copper converter (processing of brass scrap) Incineration of tyres
Sludges	Galvanising plants Wet gas cleaning plants Waste water treatment plants Phosphate treatment plants
Zinc ash	Galvanising, zinc coating plants
Refractory breaks	Various zinc producing furnaces
Metallic shredder fraction	Zinc containing fraction from car shredder
Waste from alloying processes	Scrap from die casting
External zinc scrap	Scrap from troughs, buckets, ...

Source: Rehbein [70]

### ***New Jersey retorts/gas cleaning***

Zinc oxide contained in the coked briquettes is reduced to zinc metal in the retort. For proper operation, the minimum zinc content in the input charge is between 33 - 35 %. The vertical shaft (dimensions: 10.0 x 2.0 x 0.3 m) is heated up to 1,200°C by indirect heating. At this temperature zinc metal evaporates. Re-oxidation is prevented by a surplus of CO. Process gas with its high zinc vapour and CO content leave the retort at the top. In the splash condenser zinc metal and also cadmium are condensed and subsequently transported in a launder to the feeding furnace of the refining unit. The process gas is further treated in a wet scrubbing system and burnt in the combustion chamber together with natural gas. The recovered heat is used for heating the retorts. All impurities charged with the feed mixture like lead, copper, FeO, CaO, SiO<sub>2</sub>, MgO and the surplus of carbon are concentrated in the solid residue from the retort process. For further treatment this residue is transferred to the fuming reactor plant.

### ***Refinery (New Jersey rectification)***

In the rectification column the cadmium is enriched. With the separation of a zinc-cadmium alloy, nearly cadmium-free liquid zinc is obtained. This GOB-zinc is transferred to a collecting furnace and delivered to the zinc oxide plant or for casting. In order to produce SHG zinc, remaining impurities have to be separated in the refinery. The off-gas from the heating chamber is dedusted in bag filters.

### ***Fuming reactor***

The retort residue and other zinc bearing raw materials with a low zinc content are mixed, dried and ground. This mixture is blown into the cyclone with oxygen enriched air. At temperatures of about 1,600 - 1,800°C, zinc and lead oxides are reduced to metals which evaporate in the gas phase. Combustible compounds are burnt, the remaining compounds are molten and bound in the slag. The off-gas contains mainly gaseous zinc and lead metal and carbon monoxide. With the addition of air into the post combustion chamber zinc and lead metal vapours are oxidised and carbon monoxide is burnt. The hot off-gases with a temperature of about 1,200°C are cooled down in a waste-heat boiler below 300°C. The generated steam is superheated and used in a power station. The electrical energy is used mainly for the oxygen enrichment plant, the surplus is used for other purposes. For the final cleaning and precipitation of mixed oxide a bag filter is applied. In the precipitated mixed oxide, zinc and lead are enriched up to 55 - 60 % and can be processed for zinc recovery. The slag bearing compounds form the so-called fayalite slag, which is tapped in iron crucibles at a temperature of more than 1,200°C. After cooling down over a two day period the slag is removed from the crucible. Due to the long cooling period the formation of iron-silica stones suitable for water construction is guaranteed, the slag can be sold.

### ***Induction furnace for the treatment of metallic materials***

The metallic residues as well as the scrap are remelted in an electric induction furnace. The produced zinc is collected in a segregation furnace and transported to the oxide plant. Dross removed from the segregation furnace is further treated in the retort plant.

### ***Zinc oxide plant***

In the zinc oxide plant, liquid zinc is volatilised in indirectly heated rectification columns at a temperature of roughly 1,000 to 1,100°C. To produce zinc oxide, the refined zinc vapour is burnt under controlled conditions by injection of air. For the production of zinc dust, the zinc vapour is condensed in a nitrogen atmosphere. The run-off from the rectification columns contains all metals with high boiling points like lead, iron, aluminium, tin, copper. For the recovery of these metals the run-off is returned to the segregation furnace; from time to time these metals are separated as so-called liquation lead from the furnace.

#### ***3.1.2.3.3 Summarised data on outputs and environmental concerns***

Table 3-38 shows the main controlled emissions into the air from the New Jersey retort plant.

**Table 3-38: Controlled emissions into the air from New Jersey retort plant**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [mg/Nm <sup>3</sup> ]				
		Dust	Zn	Cd	Pb	SO <sub>2</sub>
New Jersey retorts	160,000	1 - 5	0.5 - 2	< 0.001	0.1	-
Fuming plant	30,000	1 - 5	0.1 - 0.5	< 0.001	0.1	< 800
New Jersey rectification	30,000	1 - 5	0.1 - 0.5	< 0.001	0.1	-

Source: company information, company Z6, 1998

No water is discharged from the New Jersey retort plant, e.g. due to the use of cooling water circuits. Data on arising solid by-products and residues are shown in Table 3-39.

**Table 3-39: By-products and residues from the New Jersey retort plant**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
New Jersey retorts	Retort residue	20,000	Fuming plant
Fuming reactor	Slag	20,000	Sale Product
Induction furnace	Dross	1,500	Retort plant
New Jersey rectification	Zinc-cadmium alloy	20 - 100	Cadmium recovery

Source: company information, company Z6, 1998

### 3.1.2.4 Secondary zinc and zinc alloy production by remelting processes at plant Z8

#### 3.1.2.4.1 General information

Company Z8 operates a secondary zinc plant with an actual capacity of approximately 140 t per day. In addition, zinc alloys are produced. A schematic flowsheet is given in Figure 3-12.

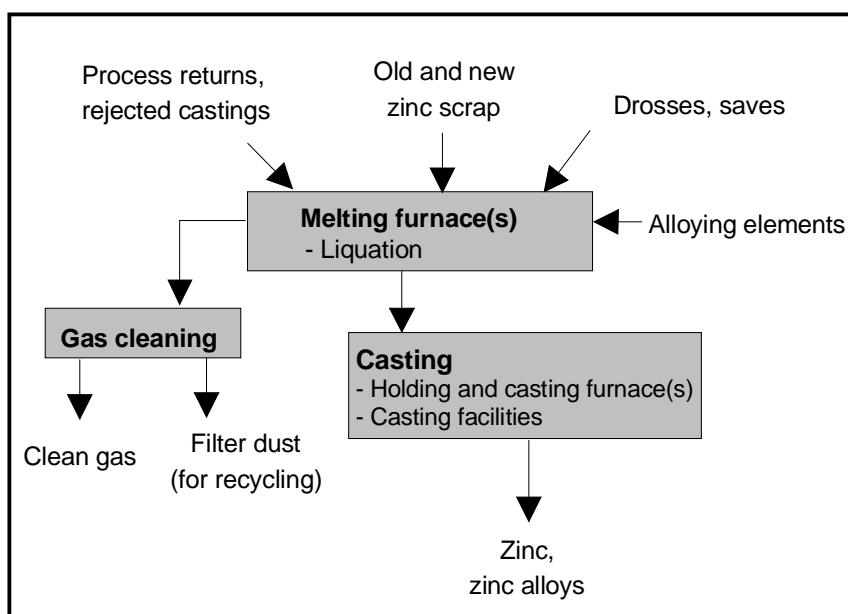


Figure 3-12: Secondary zinc production plant Z8

#### 3.1.2.4.2 Description of the main process units and environmental techniques

In the following, detailed information on the main process units of the different plants are given. Besides technical data, input and output levels and environmental measures are presented, if available.

##### Raw materials preparation

Old zinc scrap (sheets, tubes etc.) according to the European classification code word "dealer" or "Zebra", as well as new zinc scrap delivered by external manufacturers are used for the production of secondary zinc. After preparation, sampling and classification the raw materials are transferred to the melting furnaces.

Various secondary materials from the die casting industry like process returns or rejected castings are also processed. These materials are zinc alloys according to the German standard DIN 1743. In addition drosses and saves out of zinc alloys are processed. The materials are delivered separately. After sampling and classification, these fractions are also transferred to the melting furnaces.



### ***Melting furnaces***

The input charge is controlled remelted in an indirect heated melting furnace. Undesired elements can be removed in a further aggregate by partial refining. For zinc alloy production alloying components can be added to the melt after the melting process has been finished.

### ***Casting***

Liquid zinc is cast into moulds for ingots or jumbos. Zinc alloys are normally cast in standard ingots which are packed into bundles of 600 kg each. According to customers requirements, other shapes are possible. During and after the production process, the zinc and zinc alloy products are subject to a strict quality control according to European standards. It has to be guaranteed that the products conform with the required analysis or the corresponding standard.

### ***Gas cleaning***

The off-gases from the different melting units are cooled down by indirect air/air cooling and are then cleaned in bag-filters.

### ***Waste water treatment***

The company Z8 plant is operated effluent-free. There is only cooling water used for the casting equipment, which is cooled down and recirculated.

#### ***3.1.2.4.3 Summarised data on outputs and environmental concerns***

Table 3-40 shows the main controlled emissions into the air from the remelting plant.

**Table 3-40: Controlled emissions into the air from plant Z8**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [mg/Nm <sup>3</sup> ]			
		Dust	Zn	Pb	Cd
Melting furnaces	60,000	3 - 10	1.5 - 5	0.21 - 0.7	< 0.001 - 0.002
Ash production	5,000	5 - 15	0.25 - 9	0.5 - 1.5	0.001 - 0.003

Source: company information, company Z8, 1998

No water is discharged from the plant Z8. Data on arising solid by-products are shown in Table 3-41.

**Table 3-41: By-products from the remelting plant Z8**

Process unit	By-product	Amount [t/a]	Use/treatment option
Remelting	Zinc ashes	6,000	Sale Product
	Hard zinc	600	Sale Product

Source: company information, company Z8, 1998



## 3.2 Lead production in Germany

In the following, the main lead production plants operated in Germany are presented in detail. Based on the general descriptions given in Chapter 2, the processes and techniques applied are described. In addition, the present consumption and emission levels for each plant are given, where available. Due to the fact, that a strict distinction between primary and secondary process routes is not possible, in this chapter all main German production plants are included.

### 3.2.1 New direct lead smelting processes in Germany

In Germany, there are two bath smelting production plants in operation with an overall lead bullion production capacity of about 180,000 t/a lead.

#### 3.2.1.1 The QSL process (plant L1)

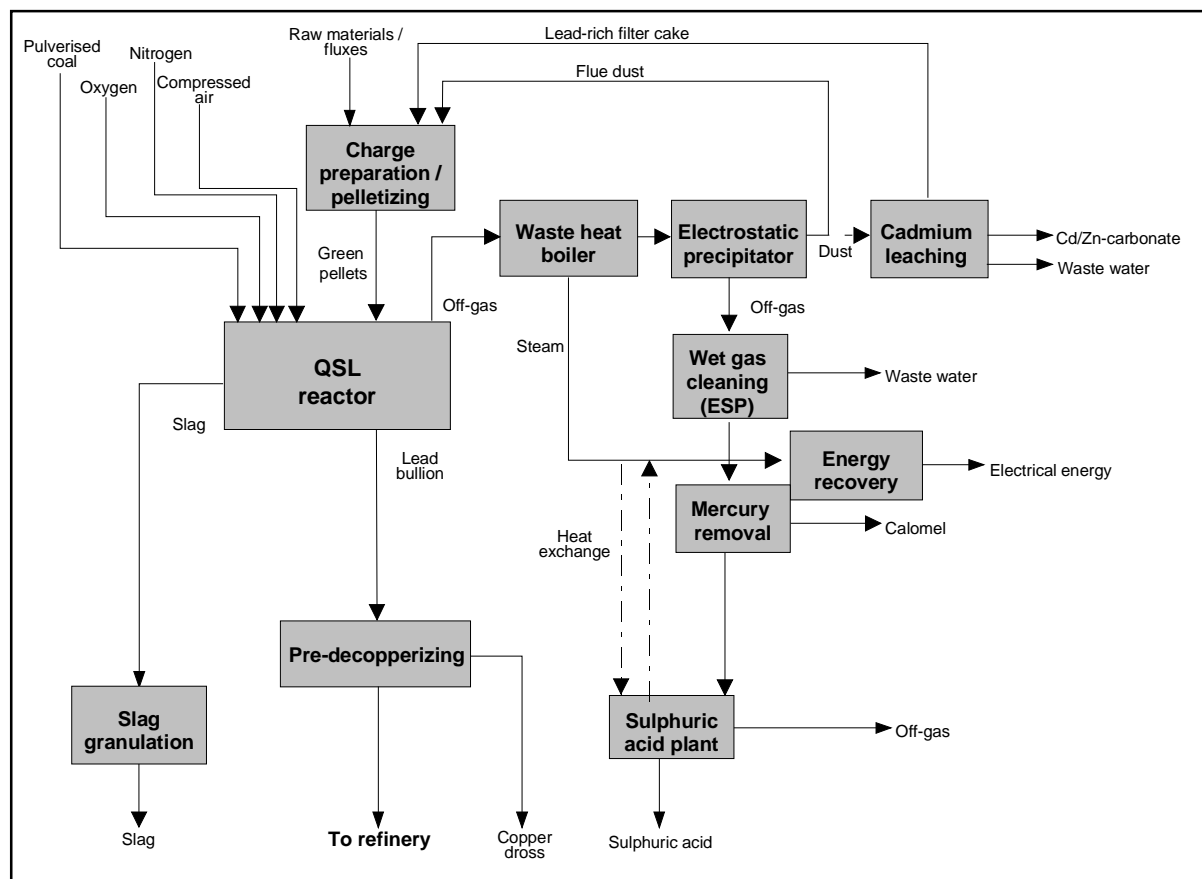
##### 3.2.1.1.1 General information

Company L1 operates a QSL plant at a location, where a conventional sinter plant - blast furnace route was replaced between 1988 and 1990. The new smelter operation started in August 1990. The QSL plant has an annual lead bullion capacity of 90,000 tons and comprises the main process units: raw material handling and charge preparation, the QSL reactor, off-gas cleaning and the sulphuric acid plant, the refining plant, and the cadmium recovery plant. A schematic view of the whole plant is shown in Figure 3-1. Table 3-42 shows input and output values of the QSL plant.

**Table 3-42: Input and output values of the QSL plant (1997)**

Input	[t/a]	Output	[t/a]
Lead-containing materials	130,000	Lead bullion	90,000
Fluxes (limestone, ...)	20,000	Slag	50,000
Nitrogen	n. a.	Sulphuric acid	60,000
Oxygen	46,000	Doré silver	250
Coal (dust)	12,000	Calomel	2 - 5
Natural gas	n. a.	Zinc-cadmium carbonate	100 - 150

Source: Company information company L1, 1998



**Figure 3-13: Process scheme of the QSL plant**

### 3.2.1.1.2 Description of the main process units and environmental techniques

In the following, detailed information on the main environmental measures in the different process units is given. Besides technical data, input and output levels are presented, where available.

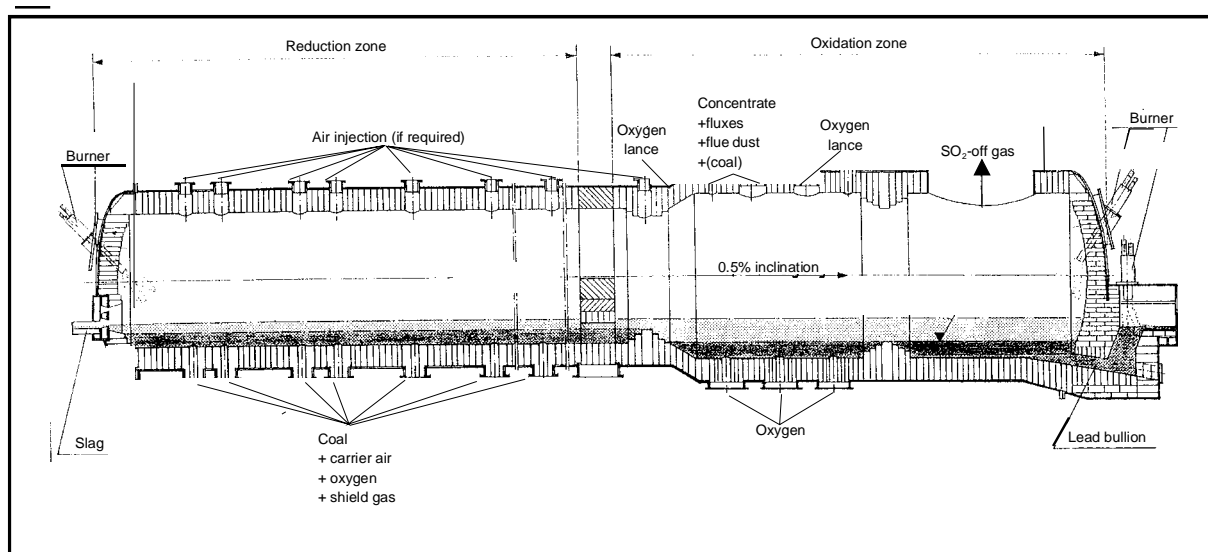
#### *Raw material handling and charge preparation*

A main advantage of the QSL technology is its flexibility concerning a variation of input materials e.g. complex lead containing materials with a high sulphur content can be processed. In 1996, the plant feed had nearly a 50:50 average ratio of concentrates to secondary material. On a monthly basis even 40:60 ratios have been achieved. Secondary materials can be the battery paste, the lead-silver concentrates from zinc plant operations, and lead scrap or lead glass. The lead concentrates, the secondary materials and the other inputs like fine coal, recycled filter cake and flue dust are pelletized in a pelletizing drum by the addition of water. For the removal of impurities and suitable slag formation, substances as lime, sand or iron oxides are added. The moist green pellets (about 13 % moisture content) are charged into the QSL reactor. On average, the feed consists approximately of 45 % lead, 5 % zinc, 0.7 % copper, 0.4 % antimony, 0.3 % arsenic, and 0.05 % cadmium [76]. Emissions from the charge

preparation and mixing are collected with hoods, and for subsequent off-gas cleaning, three different bag filters are used.

### ***QSL reactor***

The reactor is a single, closed, bath-smelting unit, which is operated in a continuous mode. The horizontal, longitudinal QSL reactor, which is shown in Figure 3-14, is subdivided by a partition wall into an oxidation zone and a slag reduction zone. The furnace is lined with chrome-magnesite bricks. The reactor has a total length of 33 m with 12.5 m smelting or oxidation zone length. It has a diameter of 3.5 m in the oxidation zone and of 3.0 m in the slag reduction zone. The oxidation zone is operated with a temperature of about 1,000°C. The pellets are charged through different openings into the oxidation zone. Oxygen is injected through tuyères directly into the bath of the oxidation zone, where lead bullion, a high lead oxide slag, and sulphur dioxide are produced. The lead bullion is tapped by a lead siphon at the bottom of the oxidation zone and poured into vessels for pre-decopperising and transfer to the refining plant. The lead oxide slag flows continuously into the reduction zone, where a temperature of up to 1,250°C is achieved.



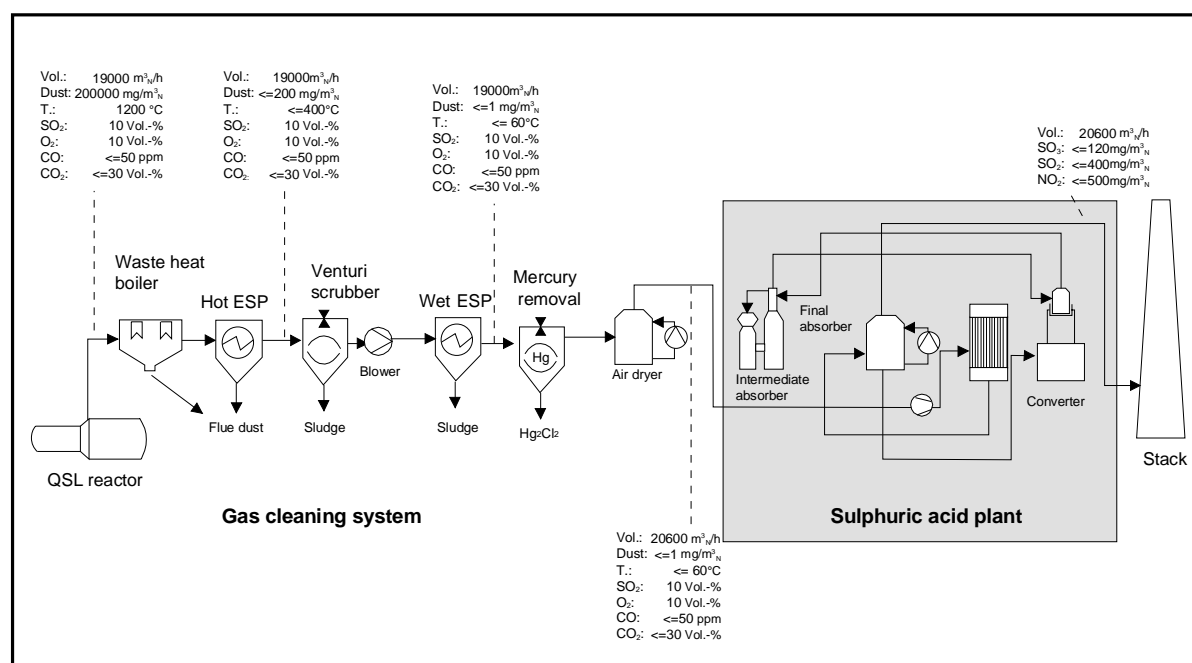
**Figure 3-14: Schematic view of the QSL reactor (planning phase)**

Source: Rentz et al. [71]

By the injection of air and pulverised coal, additional lead bullion is produced from lead oxide contained in the slag. The remaining slag with a lower lead content is tapped continuously from the reactor. The chemical reactions in the QSL reactor produce sulphur dioxide, which is collected in the off-gas stream and passed via the gas cleaning system to the sulphuric acid plant. The emissions from the lead bullion and the slag outlet are collected by hoods and complete enclosures. The exhaust gases are cleaned in three bag filters.

### Gas cleaning system/sulphuric acid plant

The off-gas (about 25,000 Nm<sup>3</sup>/h) which leaves the uptake of the reactor is first cooled down from 1,200°C to 350 - 400°C in a waste-heat boiler. The heat recovered in the waste-heat boiler is used for electric energy generation. The produced electrical energy is used for internal plant consumption. For off-gas dedusting a hot ESP is used to lower the dust content to less than 200 mg/Nm<sup>3</sup>. The collected dust contains the cadmium content of the raw materials. The dust is further treated in the cadmium leaching plant. For the final dedusting, a wet ESP is used. For the precipitation of gaseous mercury, the Norzink process is applied. Finally, the purified off-gas with an average sulphur dioxide content of 10 % is treated with double absorption contact<sup>18</sup> to sulphuric acid. The off-gas is then released into the atmosphere via a stack. The sulphuric acid produced contains less than 0.5 g mercury/t. A schematic overview of the different gas cleaning devices and their cleaning efficiency is given in Figure 3-15. Annual average off-gas values are given in Table 3-44.



**Figure 3-15: Gas cleaning system of the QSL plant**

Source: Deininger et al [20]

### Slag granulation

The slag is treated with high pressure water in the slag granulation unit. The off-gases from the slag granulation stage are captured by hoods and finally dedusted in a wet ESP. The chemical composition of the granulated slag and its eluate are given Table 3-43.

<sup>18</sup> In Germany, both plants, which process lead ore concentrates operate double absorption contact plants. Further information on the process technology in general can be found elsewhere e.g. VDI [97], Rentz et al. [71].

**Table 3-43: Average analysis of the QSL slag**

<b>Compound</b>	<b>Granulated slag [wt.-%]</b>	<b>Eluate<sup>1)</sup> [mg/l]</b>
As	0.2	0.05
Cd	0.002	0.001
Cr	n. a.	n. a.
Cu	0.2	0.005
Hg	n. a.	n. a.
Ni	n. a.	n. a.
Pb	1 - 3	0.05 - 0.2
Zn	10	n. a.
FeO	25	0.01
CaO	15	n. a.
MgO	4	n. a.
Al <sub>2</sub> O <sub>3</sub>	3	n. a.
SiO <sub>2</sub>	19	n. a.

<sup>1)</sup> : According to the German Eluattest DEV S4 (c.f. Deininger et al. [20])

### ***Cadmium leaching plant***

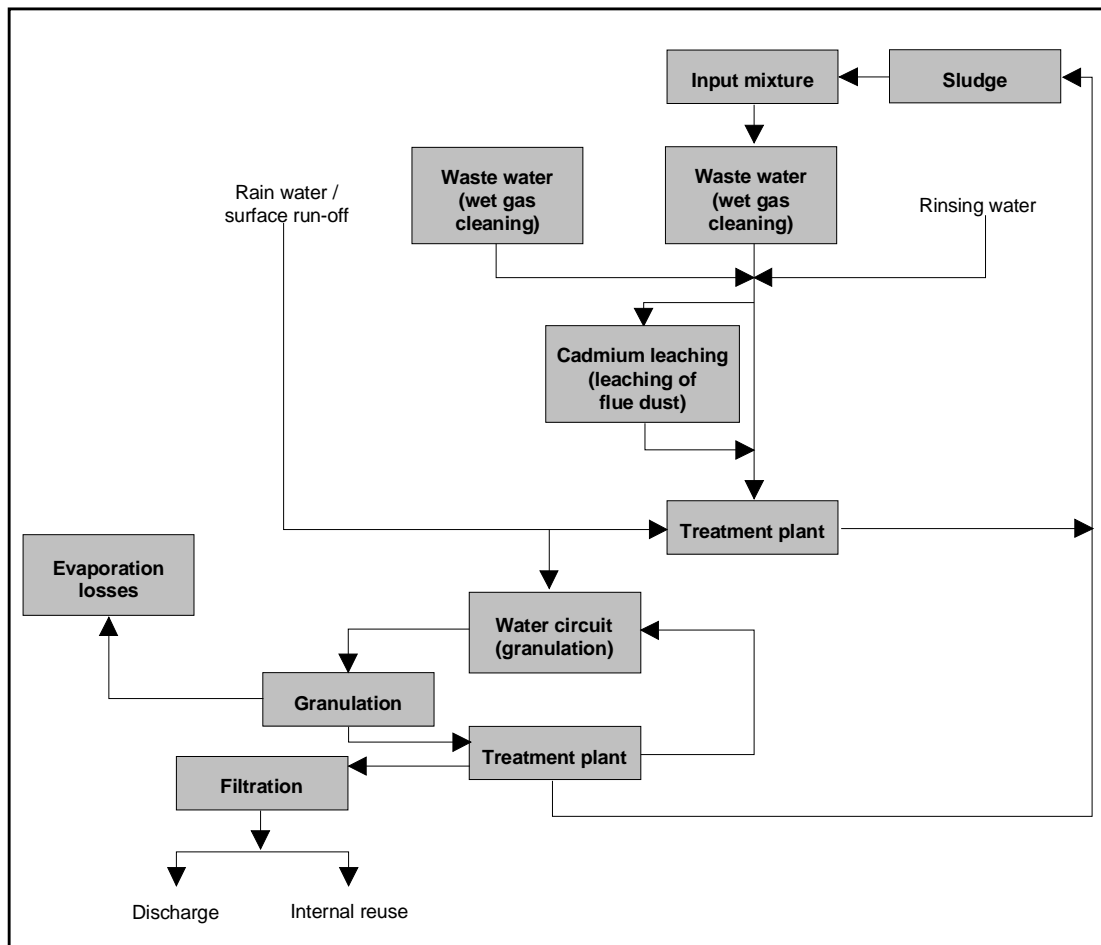
The flue dust separated from the furnace off-gas in the hot ESP contains most of the cadmium charged with the inputs. In order to recover the cadmium, the ESP dust is leached. The cadmium rich solution is separated from the solids by filtration, and the filter cake is reprocessed. In a second step, a zinc-cadmium carbonate (cadmium content: 30 – 35 wt.-%; zinc content: 15 – 25 wt.-%) is precipitated by the addition of sodium carbonate solution.

### ***Refining plant***

In the refining plant equipped with 21 kettles the crude lead is refined (c.f. the description of refining processes in Section 2.2.2.5) and alloyed to the required product qualities. The produced lead and lead alloys are cast into ingots and blocks (50 – 3,000 kg) [9]. The emissions from the refining kettles are collected by hoods connected to a ventilation system. For emission control, bag filters are used.

### ***Water management/waste water treatment***

In Figure 3-16, the water circuits of the QSL plant are shown.

**Figure 3-16: Schematic view of the water circuits in the QSL plant**

Source: Deininger et al. [20]

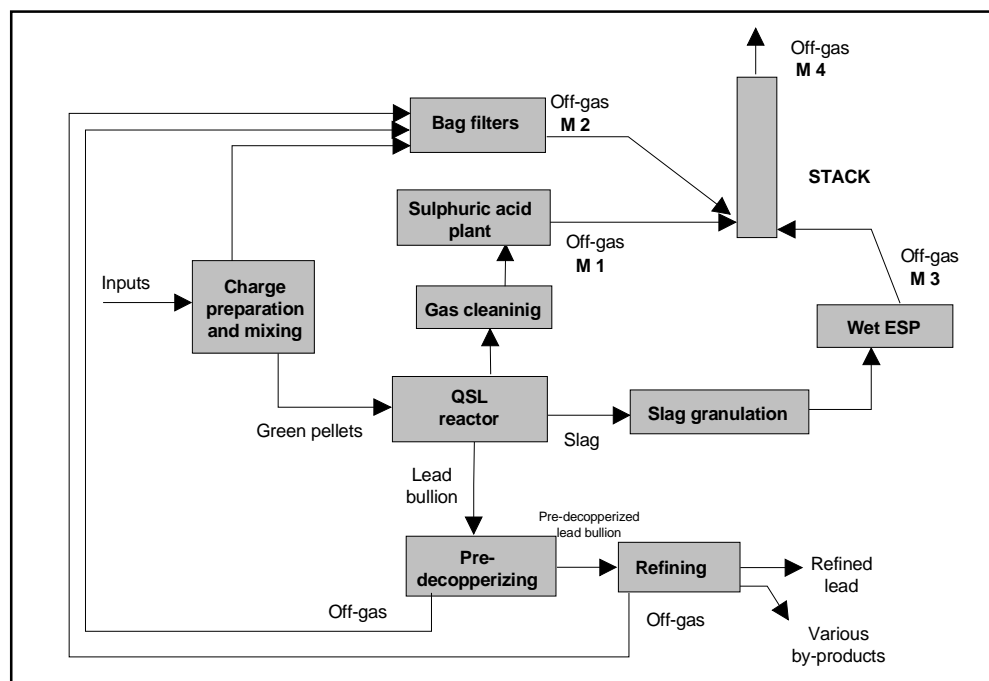
The cooling circuit has a capacity of 2,000 m<sup>3</sup>/h. The process water is used internally to reduce water consumption. A central water treatment plant is operated. Due to the cadmium recovery from products, the central treatment plant is relieved of this substance. The discharged waste water fulfils by far the requirements of German waste water regulations.

### 3.2.1.1.3 Summarised data on outputs and environmental concerns

#### *Emissions into the air*

Figure 3-17 shows the main emissions sources of the QSL plant (M1-M4).





**Figure 3-17: Main sources of controlled emissions (QSL plant)**

An overview of controlled emissions from the QSL plant is given in Table 3-44.

**Table 3-44: Controlled emissions into the air from the QSL plant (annual average values)**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components (mg/Nm <sup>3</sup> )				
		Dust	Pb	Cd	SO <sub>2</sub>	NO <sub>x</sub>
Raw material storage/ handling/refinery	220,000	1 - 2	0.2 - 1	0.005 - 0.05	20 - 200	10 - 20
Clean gas (sulphuric acid plant)	20,000	< 1	0.001 - 0.02	0.001 - 0.002	200 - 300	250 - 400
Slag granulation	190	1 - 5	0.5 - 2	< 0.001	< 20	< 10

Source: company information company L1, 1998

The content of PCDD/PCDF in the off-gases is less than 0.1 ng-TE/Nm<sup>3</sup>. Compared to the traditional lead production with the main emission sources sinter plant and blast furnace, the QSL plant is a low emission potential process as shown in Table 3-45. For example, the sulphur dioxide emissions into the air are considerably lower than from the conventional sinter plant - blast furnace route. In addition, a reduction of lead emissions to air has been achieved from 140 g/t lead for the conventional plant compared to 40 g/t lead for the QSL plant [7].

**Table 3-45: Comparison of controlled emissions from lead bullion production (QSL plant/conventional plant)**

Components	QSL plant*) [t/a]	Conventional plant*) [t/a]	Reduction rate [%]
Dust	12.5 <sup>1)</sup>	20.2	38
Lead, total	5.2 <sup>1)</sup>	8.4	38
<i>Process off-gas</i>	0.154 <sup>1)</sup>	2.1 <sup>2)</sup>	92.5
Cadmium, total	0.025 <sup>1)</sup>	0.17	85
<i>Process off-gas</i>	0.0167 <sup>1)</sup>	0.25 <sup>2)</sup>	93
Zinc	0.65 <sup>1)</sup>	1.3	49
Arsenic	0.072 <sup>1)</sup>	0.12	38
Sulphur dioxide, <i>process off-gas</i>	89 <sup>1)</sup>	2970	97

\*) The calculations have been done for the same installed raw material capacity of 150,000 t/a

Source: <sup>1)</sup> Deininger [19]; <sup>2)</sup> Deininger et al. [20]

### ***Waste water***

In Table 3-46 data on waste water from the QSL plant is summarised.

**Table 3-46: Data on waste water from the QSL plant (annual average values)**

Process unit	Effluent [m <sup>3</sup> /a]	Flow [m <sup>3</sup> /h]	Main components [mg/l]						
			Pb	Cd	As	Zn	Ni	AOX	COD
Waste water treatment plant	90,000	10	0.1	< 0.05	< 0.05	0.3	< 0.05	< 0.1	20

Source: company information company L1, 1998

### ***By-products and residues***

The granulated QSL furnace slag is of the iron silicate type with a slag basicity of 0.8 - 1.0. It has a zinc content of up to 15 % and can be used externally for different options e.g. in road construction [9]. The flue dust from the waste-heat boiler and the hot ESP is recirculated internally to charge preparation. To prevent cadmium enrichment in the process a certain amount (16 t dust per day) is continuously discharged and treated in a cadmium leaching plant. The recovered zinc-cadmium carbonate is dumped. Silver and other noble metals are recovered from lead bullion during refining and then sold. An overview of the by-products and residues is given in Table 3-47.

**Table 3-47: By-products and residues from the QSL plant**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Slag treatment	Granulated slag	50,000	Used in certain road construction fields
Gas cleaning system	Filter dust	n. a.	Recycling to smelting reactor Cadmium/chlorine removal
	Calomel	2 - 5	Saleable by-product
	Waste heat	n. a.	Power generation or turbines
Sulphuric acid plant	Sulphuric acid	60,000	Saleable by-product
Refinery	Doré metals (silver, ..)	250	Treated and/or sold
Cadmium leaching	Zinc - cadmium carbonate	100 - 150	Dumping
Waste water treatment plant	Sludges	n. a.	Dumping

Source: company information company L1, 1998

### ***Other environmental concerns***

The dust immisions in the vicinity of the plant L1 are shown in Table 3-48.<sup>19</sup>

**Table 3-48: Dust immissions in the vicinity of the QSL plant (examples, 1991)**

Element	Content in the suspended dust formation [µg/Nm³]	Content in the dust sediment [µg/m²d]	Source
Lead	0.1 - 0.5 <sup>1)</sup>	120 <sup>2)</sup>	[20]
Cadmium	0.002 - 0.005 <sup>1)</sup>	5 <sup>2)</sup>	[20]

<sup>1)</sup>: The given range is valid for three different measurement stations in 1991.

<sup>2)</sup>: These values are mean values of 24 measurement stations in 1991.

In the context of the plant modernisation, extensive investigations were performed to compare the former conventional lead production plant with the new QSL plant. Table 3-49 shows the energy-losses due to not-used heat streams in a QSL plant and in a conventional plant which shows a 50 % reduction in the QSL plant.

<sup>19</sup> A detailed description of the determination of the emissions from the QSL plant and the immissions in the vicinity of the plant is given in Deininger et al. [20].

**Table 3-49: Comparison of not-used energy streams (QSL plant/conventional plant)**

Heat stream	QSL plant [GJ/h]	Conventional plant [GJ/h]
Cooling water and radiation (wall)	12.00	30.50
Off-gas	10.25	28.50
Sensible heat (lead)	1.45	1.45
Sensible heat (slag)	9.25	9.25
Sensible heat (sinter)	-	8.70

Source: Deininger et al. [20]

Concerning *energy consumption*, the following comparisons can be made: Compared to conventional lead bullion production (sinter plant - blast furnace route) with a specific energy consumption of about 10,000 MJ/t Pb, a reduction of 30 % in the QSL plant can be achieved. As shown in Table 3-50, the specific energy input per ton of raw material input in a QSL plant is about 3,600 MJ including a credit for generated energy by the waste-heat boiler steam, whereas a conventional plant requires about 5,150 MJ.

**Table 3-50: Consumption of primary energy (QSL plant/conventional plant)**

Energy source	QSL plant <sup>*)</sup> [MJ/t raw material input]	Conventional plant [MJ/t raw material input]
Electricity	-	938
Natural gas	741.5	348.5
Coal dust	2552	-
Coke	-	3848
Oxygen <sup>**) </sup>	360	13
<b>Sum</b>	<b>3653.5</b>	<b>5147.5</b>

\*) These values were determined at the plant site in 1992.

\*\*) This value gives the amount of electrical energy required for oxygen production.

Source: Deininger et al. [20]

### 3.2.1.2 The Sirosmelt process (plant L2)

#### 3.2.1.2.1 General information

Company L2 operates a Sirosmelt process plant. This technology has replaced a conventional sinter plant - blast furnace route in the end of 1995. The Sirosmelt plant, shown schematically in Figure 3-18, consists of the following main process steps: the storage of raw materials and the charge preparation, the Sirosmelt reactor, the gas cleaning system, the sulphuric acid plant, the refining plant and the devices for slag processing.

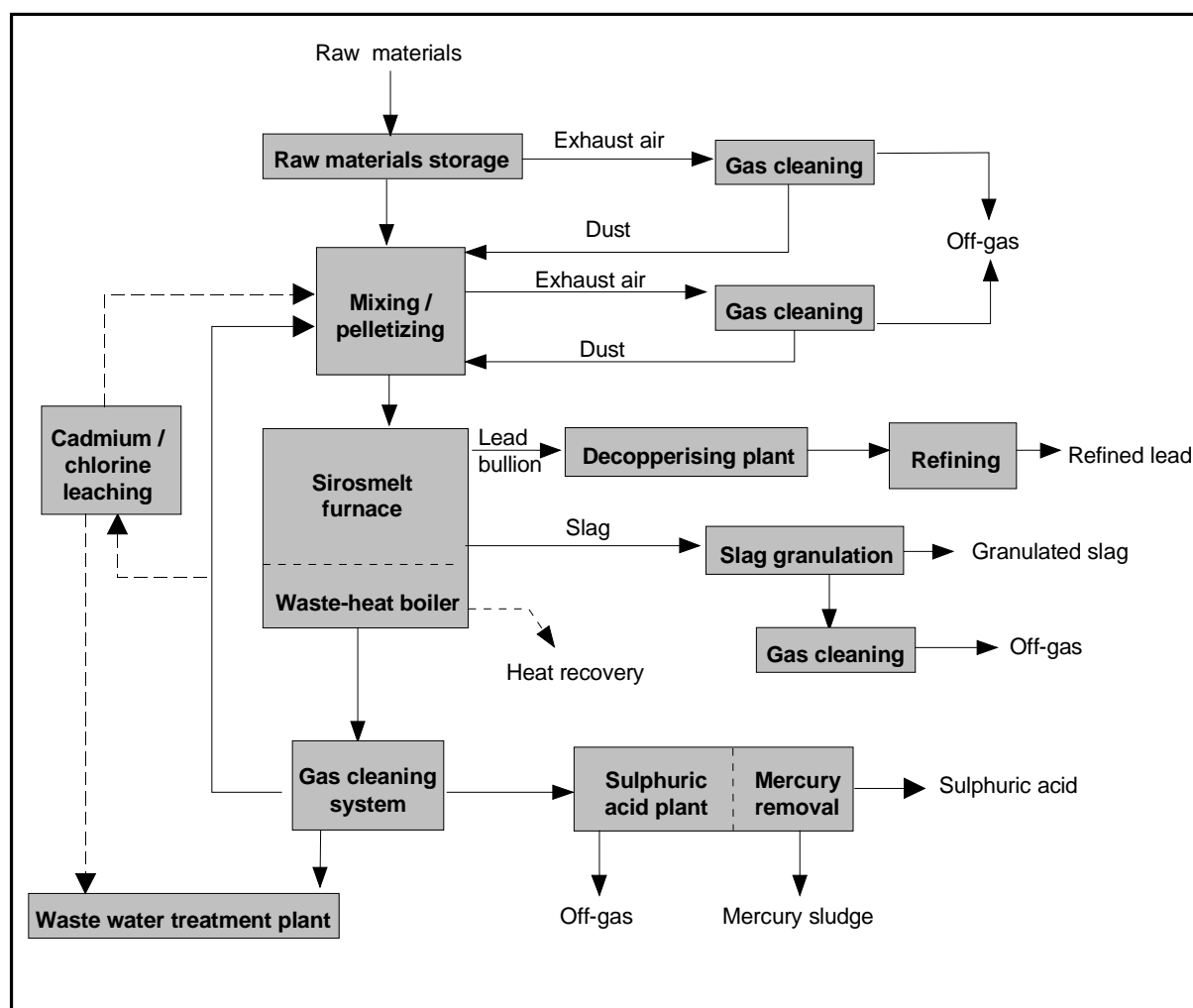


Figure 3-18: Sirosmelt plant L2

In Table 3-51, input and output values of the Sirosmelt plant are given.

**Table 3-51: Input and output values of the Sirosmelt furnace (project figures)**

Input	[t/a]	Output	[t/a]
Battery lead paste, others	82,000	Lead	90,000
Lead concentrates	40,000	Sulphuric acid	25,000
Recycled flue dusts	34,000	Slag	10,000
Fluxes	3,500	Mercury residue	20
Coal or coke	7,100	Flue dust (recycled to the furnace)	34,000
Oxygen	13,300		

Source: company information company L2, 1998

### ***3.2.1.2.2 Description of the main process units and environmental techniques***

In the following, information on the main environmental measures in the different process units is given. Besides technical data, input and output levels are presented, where available.

#### ***Raw materials***

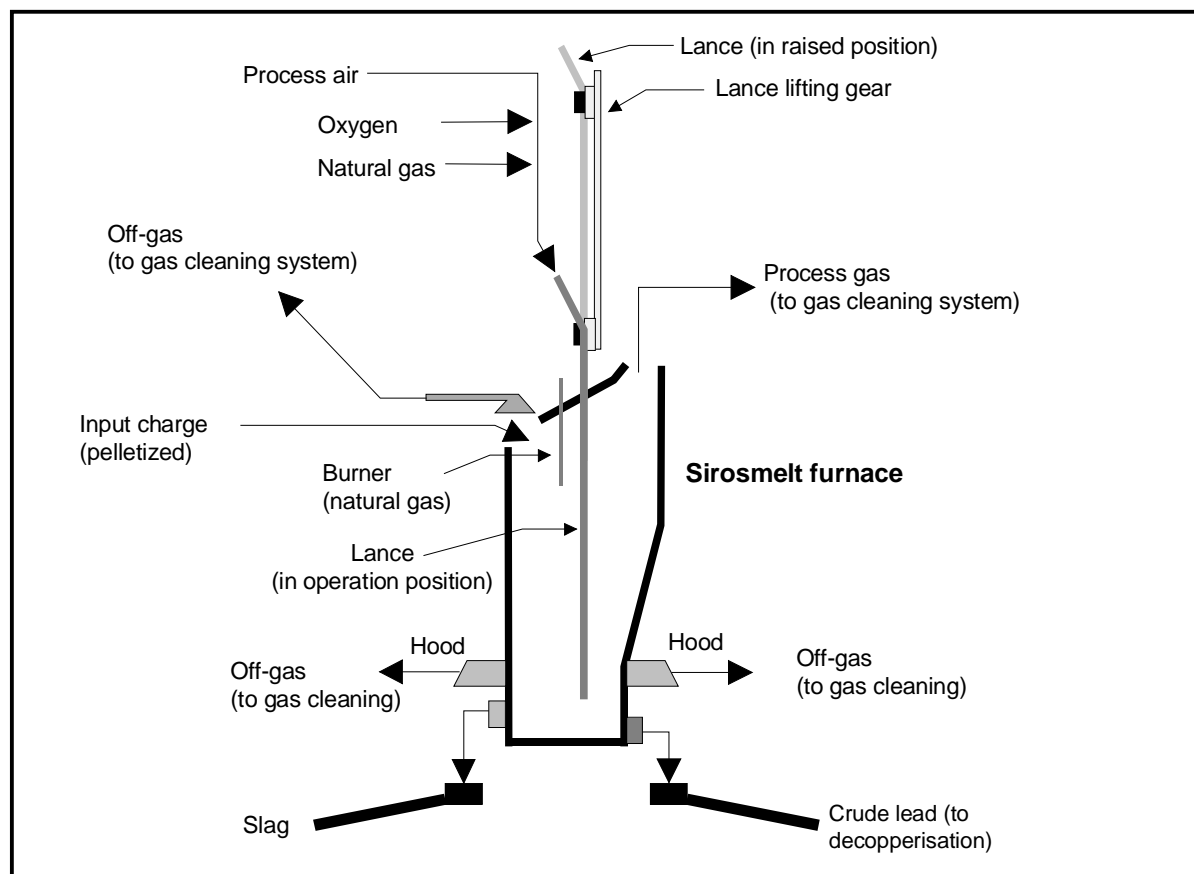
The input materials are the oxide-sulphate fraction of recycled lead-acid batteries and lead concentrates, which are stockpiled in a totally closed building. For the comminution of coarse materials, a rebound crusher with intermediate sieving is available. All storage devices (crushers, bins, ...) are closed and equipped with suction hoods. The gas cleaning devices have a capacity of 87,000 Nm<sup>3</sup>/h. The raw material is transferred to the dosing bins with a new closed belt conveyor to prevent fugitive dusting.

#### ***Mixing and pelletizing of inputs***

For mixing and pelletising, the raw materials are transferred to the pre-treatment unit. Subsequently water is added to achieve the humidity for pelletising and then pellets are formed. All emission relevant parts are captured and connected to a gas cleaning device with an air suction capacity of 30,000 Nm<sup>3</sup>/h.

#### ***Sirosmelt furnace (including the pre-decopperising unit)***

The Sirosmelt process is carried out in a stationary smelting furnace equipped with a blowing lance as shown in Figure 3-19.



**Figure 3-19: Schematic view of the Sirosmelt furnace**

The height of the furnace is about 10 m with an inner diameter of 3.5 m. The furnace walls are cooled on the outer surface by water sprinkling, the inner side is refractory lined. The furnace is operated with two different campaigns: the smelting and the reduction campaign. For smelting, the raw material pellets are continuously charged into the furnace via a conveyor belt. A moveable lance is used to inject natural gas, oxygen and air into the bath. In the reducing atmosphere, the input charge is melted. In the roast reaction lead sulphides contained in the input charge react to liquid metallic lead and sulphur dioxide. A temperature of between 1,000°C and 1,100°C is obtained. A liquid lead phase and a liquid slag phase are achieved and continuously tapped. The process gases coming up from the bath are post combusted in the furnace gas atmosphere. At the resulting high temperatures, organic substances contained in the process gas like PCDD/PCDF are destroyed. The produced lead bullion is tapped continuously and led to the decopperising plant. The slag with a high lead content of up to 55 % is tapped, stored and further processed in the reduction campaign. This campaign is carried out discontinuously or continuously in the same furnace, if a certain amount of slag has been collected and the smelting campaign is finished.

Within the reduction campaign, the slag from the smelting campaign and reducing agents like coal or coke are charged into the furnace. At temperatures of about 1,250°C additional lead bullion is produced and subsequently tapped. The lead content of the slag is reduced to 8 - 10 %. In the final fuming step, the lead but also the zinc content is lowered further by blowing

of oxygen and coal into the furnace. Lead and zinc oxide containing flue dust is generated, collected in the process gas, precipitated in the gas cleaning system and intended for sale (e.g. zinc recovery).

The decopperising of lead bullion is carried out in kettles. While the lead bullion cools, copper and other impurities separate as a lead-rich copper dross which is skimmed off. After Colcard decopperisation, the lead bullion is transferred to the refining plant.

To prevent emissions into the air, the charging and the tapping area are equipped with hoods. The exhaust air is cleaned with bag filters.

### ***Gas cleaning system (Sirosmelt furnace)***

The process gases are treated in a multistage gas cleaning system. First, the off-gases are cooled down in a waste-heat boiler following the circulating fluidised bed principle. The hot dust containing off-gas, which reaches the mixing chamber, is cooled down to 300 - 450°C immediately by recirculated flue dust. The recovered sensible off-gas heat is used for steam generation or water heating. In the next step, cyclones are used for coarse dust precipitation down to 30 - 45 g/Nm<sup>3</sup>. Precipitated dust which is not recirculated for cooling, is recycled to the charge preparation unit. Subsequently, the off-gas (200 - 350°C) is cleaned in two ESP and a Venturi scrubber for further dedusting. For final purification, another gas cooler and a two-stage wet ESP are used.

### ***Sulphuric acid plant/mercury removal***

A double absorption contact plant is in operation to produce sulphuric acid by converting sulphur dioxide contained in the off-gas. Due to the fact, that several process steps are carried out in the reactor, the sulphur dioxide content varies considerably over time. For example, during smelting a high sulphur dioxide content is expected, but during reduction the content should be much lower. To permit efficient and stable contact plant operation, the off-gas is mixed with the off-gas from a neighbouring fluid bed zinc roaster. This ensures that the sulphur dioxide content is high enough for the double contact absorption plant. The acid from the drying steps collects the mercury of the process gases and is treated by using the Boliden Chemie process. Mercury is removed as a sludge by filtration of the acid. The sulphuric acid produced contains less than 0.5 g mercury/t.

### ***Leaching of flue dust***

As most of the flue dust is recycled to the input mixing unit, cadmium and chlorine removal by leaching of flue dust may be necessary from time to time.



### ***Refining plant***

Lead bullion from the Sirosmelt furnace and purchased lead bullion from external smelters is refined in different steps, alloyed if necessary and cast into ingots of 50 kg weight. Therefore, the equipment of the refining plant consists of the following kettles and furnaces:

- 15 kettle furnaces with capacities between 100 t and 200 t,
- three liquation furnaces
- a Leferrer vacuum dezincing furnace, and
- a cupellation furnace.

The kettles and furnaces are covered with hoods which are ventilated via a central bag filter with an off-gas capacity of 80,000 Nm<sup>3</sup>/h.

### ***Slag granulation***

After tapping, the slag is immediately granulated. The slag granulation is carried out with water and a redler equipped sedimentation basin is used for the separation of water and slag. During slag granulation, wet waste gases are emitted containing e.g. heavy metal dusts and vapours. These gases are captured with a volume of up to 13,000 Nm<sup>3</sup>/h and are cleaned in a wet ESP.

### ***Water management/waste water treatment***

The waste water plant is used for the treatment of waste water not only from the lead plant but also from the neighbouring zinc electrolysis plant.

#### ***3.2.1.2.3 Summarised data on outputs and environmental concerns***

### ***Emissions into the air***

Table 3-52 shows the main controlled emissions into the air from the Sirosmelt plant. The main sources for emissions are the two or three tapholes, the exhaustion of machinery and the various slag and metal runners. Due to extensive capturing devices for storage and raw material transport, mixing and pelletising, total dust emissions are lowered e.g. for lead by 83 %.

**Table 3-52: Controlled emissions into the air from the Sirosmelt plant (1997)**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components (mg/Nm <sup>3</sup> )				
		Dust	Pb	Cd	SO <sub>2</sub>	NO <sub>x</sub>
Raw material storage/handling	118,000	< 0.5	< 0.1	< 0.01	-	-
Clean gas (sulphuric acid plant)	35,000	-	-	-	300 - 1,300	15 - 52
Slag granulation/furnace area	110,000	1 - 2	< 1	< 0.01	-	-
Refinery	66,000	< 0.5	< 0.3	< 0.01	-	-

Source: company information company L2, 1998

Compared to the conventional lead smelting route, a main feature of the Sirosmelt technology is the significantly lower sulphur dioxide emission (about 90 % lower). Table 3-53 shows the emission reduction achieved by plant modernisation at the plant site between 1990 and 1997.

**Table 3-53: Emission reduction achieved by plant modernisation**

Emissions	Conventional plant (1990) [kg/a]			Sirosmelt plant (1997) [kg/a]			Reduction rate [%]		
	Controlled	Fugitive	Total	Controlled	Fugitive	Total	Controlled	Fugitive	Total
Lead	5,236	19,555	24,791	911	540	1,451	83	97	94.1
Cadmium	330	242	572	3.81	0.24	4.05	99	> 99	99.3
Antimony	151	309	460	25.8	1.77	27.52	83	> 99	94
Arsenic	77.6	141.5	219.1	4.03	1.55	5.58	95	99	97.5
Thallium	21.9	16.1	38	1.27	< 0.01	1.27	94	> 99	96.7
Mercury	16.7	0.4	17.1	0.87 <sup>*)</sup>	< 0.01	0.87	95	> 97	95
Sulphur dioxide [t/a]	7,085	-	7,085	140.4	-	140.4	98	-	98

<sup>\*)</sup> The controlled mercury emissions from the Sirosmelt plant are given for 1996.

Source: Klotz [40], company information company L2, 1998

### Waste water

For the treatment of waste water, a central treatment plant is operated together with a neighboured zinc electrolysis plant. In Table 3-54 data on waste water discharged from this plant is summarised.

**Table 3-54: Data on waste water from the Sirosmelt plant**

Process unit	Effluent [m <sup>3</sup> /a]	Flow [m <sup>3</sup> /h]	Main components [mg/l]				
			Pb	Cd	As	Zn	AOX
Waste water treatment plant	340,000	45 - 50	0.01 - 0.09	0.001 - 0.01	0.001 - 0.1	0.01 - 0.2	0.004 - 0.2

Source: company information company L2, 1998

**By-products and residues**

An overview of the by-products and residues is given in Table 3-55.

**Table 3-55: By-products and residues from the Siros melt plant**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Gas cleaning system	Filter dust	34,000 <sup>*)</sup>	Internal recycling to reactor
Cadmium/chlorine leaching	ESP dust	n. a.	Internal recycling
Sulphuric acid plant	Sulphuric acid	25,000	Saleable by-product
	Mercury residue	20	Internal recycling
Slag treatment	Granulated slag	10,000	Road construction, concrete
Waste water treatment plant	Sludges	200 <sup>**) </sup>	Dumping

<sup>\*)</sup> About 20% of the dust are leached; the arising filter cake is also recycled to the reactor.

<sup>\*\*)</sup>  In this value, the zinc smelter waste water residue is contained.

Source: company information company L2, 1998



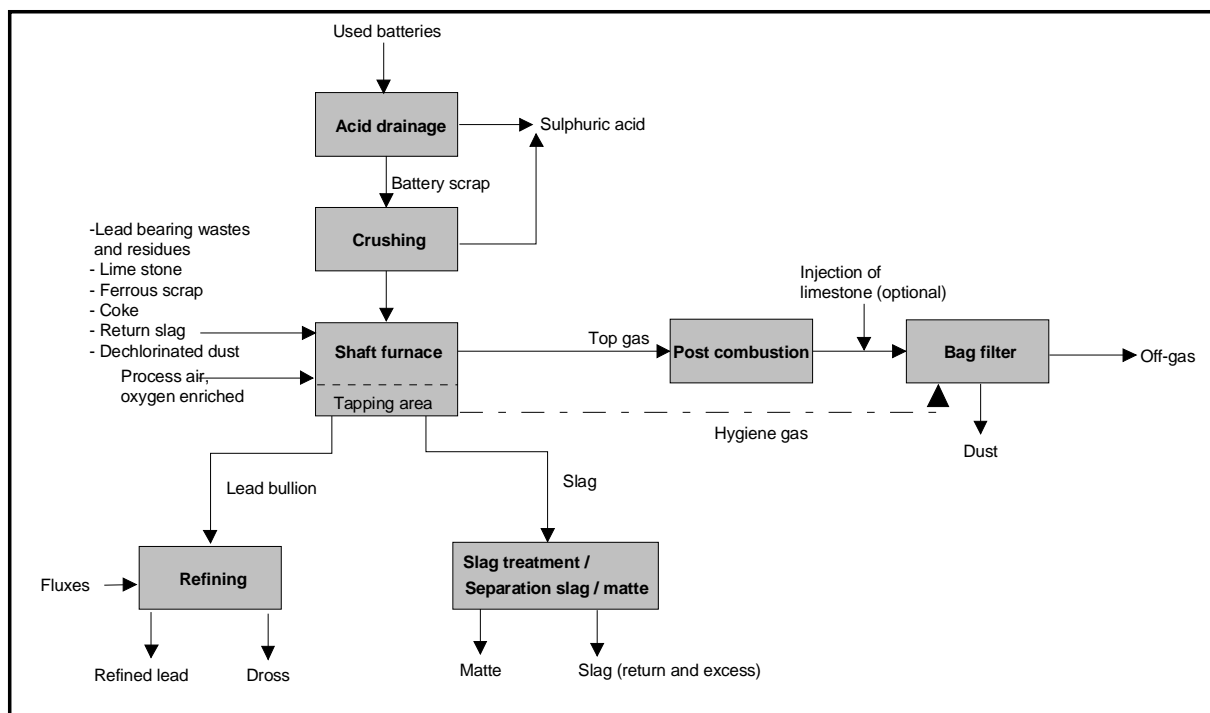
### 3.2.2 Lead recycling from secondary raw materials using a shaft furnace (plant L5)

#### 3.2.2.1 General information

Company L5, a subsidiary of a battery producing company operates a recycling plant for used lead-acid batteries [91]. The process uses a shaft furnace to process whole batteries after the removal of acid. A schematic view of this process is given in Figure 3-20. As shown, the plant can be subdivided into the following production units:

- a shaft furnace with an annual production capacity of 35,000 tons crude lead, and
- refining and alloying processes.

This process is also operated in other European countries e.g. in Belgium, the Czech Republic, Russia and Sweden. The whole plant is already certified according to ISO 9002; while the certification according to the ISO 14001 and the EMAS will follow in 1998. In the following the shaft furnace process and the subsequent refining and alloying steps are discussed in detail.



**Figure 3-20: Shaft furnace plant L5 for recycling of lead-acid batteries**

Table 3-56 gives an overview of the main input and output values in order to provide a first characterisation of this process.

**Table 3-56: Main input and output values from the shaft furnace recycling plant (1997)**

Input	[t/a]	Output	[t/a]
Old batteries, dry	33,000	Crude lead	30,000
Other lead scrap, waste	9,600	Flue dusts	950
Fluxes (limestone)	450	Excess slag	1,500
Coke (foundry coke)	3,600	Return slag	16,000 - 18,000
Other inputs (iron)	2,000	Iron/lead matte	4,200
Slag (return)	n. a.	Used sulphuric acid	3,350
Oxygen	1.3 Mio. Nm <sup>3</sup>		
Lead carbonate (from flue dust treatment)	1,200		
Natural gas	450,000 m <sup>3</sup>		
Electrical energy	3.200 MWh		

Source: company information company L5, 1998

### 3.2.2.2 Description of main process units and environmental techniques realised

In the following, detailed information on the main environmental measures in the different process units is given. Besides technical data, input and output levels are presented, where available.

#### *Raw material handling*

First of all, the delivered batteries are crushed in order to remove the liquid acid, then they are stored in the storage yard. The battery scrap and other lead bearing wastes are mixed with additions as coke, limestone, iron scrap and return slag. To prevent fugitive non-captured dust emissions from storing, transport and handling, most input materials are moistened. As mentioned above, the waste battery acid is separated from the battery scrap. After a filtering step, it can be used for some applications replacing virgin sulphuric acid, e.g. for zinc leaching in zinc electrolysis or for waste water neutralisation in water treatment plants.

#### *Shaft furnace*

The charge is fed directly into the shaft furnace using a shovel loader. The shaft furnace has a height of about 8 metres. It runs continuously in order to maintain stable conditions to produce a consistently high quality and a sound environmental performance. The furnace is relined less than once a year. To reduce and smelt the charge, oxygen enriched air is injected into the furnace. The produced lead bullion is tapped into a mould and cooled down for further treatment. The shaft furnace slag is tapped in special slag pots. In order to collect the emissions from tapping, secondary hoods are installed. After slow solidification, the iron, lead and sulphur containing matte can be separated from the Iron silicate slag. The matte is treated externally to recover sulphur, lead and copper. A typical composition of the shaft furnace slag is given in Table 3-57.

**Table 3-57: Typical composition of shaft furnace slag**

Compound	FeO	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	Pb
[wt.-%]	30 - 40	25 - 35	15 - 25	5 - 15	1 - 2

Source: company information company L5, 1998

The plastic materials contained in the inputs are volatilised in the upper zone of the furnace and leave the furnace with the off-gas. Other emissions from the process e.g. gaseous and particulate heavy metal emissions, are effectively collected together with the off-gas stream, and are then passed to the post combustion chamber of the gas cleaning system. Apart from the water for cooling purposes, no process water is used in the company L5 shaft furnace process itself. The specific input and output values of the shaft furnace process are given in Table 3-58.

**Table 3-58: Specific input and output values of the shaft furnace plant L5 (1997)**

Input	[kg/t lead bullion]	Output	[kg/t lead bullion]
Used batteries, dry	1100	Lead bullion	1,000
Other lead scrap, waste	320	Flue dusts	32
Fluxes (limestone)	14	Excess slag	50
Coke (foundry coke)	109	Return slag	n. a.
Other inputs (iron)	67	Off-gas	18,200 Nm <sup>3</sup>
Lead carbonate (from flue dust treatment)	40	Iron/lead matte	140
Slag (return)	n. a.		
Oxygen	43 Nm <sup>3</sup>		
Natural gas	15 Nm <sup>3</sup>		
Electrical energy	107 kWh		

Source: company information company L5 (1998)

### ***Gas cleaning system***

In order to prevent organic emissions, a post combustion chamber has been installed for burning combustible components. In this chamber, the gas is ignited by natural gas burners and burnt at temperatures of up to 1,100°C to remove any remaining hydrocarbons. The arising hot off-gases are cooled down rapidly (dry quenching) with the secondary off-gases and cleaned in a fabric filter. A dust content in the clean gas below 1 mg/Nm<sup>3</sup> is achieved. A typical composition of cleaned off-gas is given in Table 3-59.

**Table 3-59: Typical data of the cleaned shaft furnace off-gas**

Substance in the off-gas <sup>*)</sup>	Content
Dust load [mg/Nm <sup>3</sup> ]	< 1.0
Lead [mg/Nm <sup>3</sup> ]	< 0.5
Cadmium [mg/Nm <sup>3</sup> ]	< 0.05
Carbon <sub>total</sub> [mg/Nm <sup>3</sup> ]	< 10
Sulphur dioxide [mg/Nm <sup>3</sup> ]	< 500
Nitric oxide (NO <sub>x</sub> as NO <sub>2</sub> ) [mg/Nm <sup>3</sup> ]	< 50
Carbon monoxide [mg/Nm <sup>3</sup> ]	< 50
Hydrochlorine (HCl) [mg/Nm <sup>3</sup> ]	< 5
Hydrofluorine (HF) [mg/Nm <sup>3</sup> ]	< 0.5
PCDD/PCDF (Σ TE, NATO) [ng-TE/Nm <sup>3</sup> ]	< 0.1

<sup>\*)</sup> Off-gas stream: 65,000 Nm<sup>3</sup>/h

Source: company information company L5, 1998

The off-gas amounts to 65,000 Nm<sup>3</sup>/h. Emissions as dust, carbon monoxide and sulphur dioxide are monitored continuously. Calcium hydroxide additive can be injected into the off-gas channel, to prevent sulphur dioxide emissions peaks. The fabric filter dust has a lead content of up to 65 wt-% and can be recycled back to the smelting furnace as input material after chlorine removal. In order to achieve this, the filter dust is treated externally in a hydro-metallurgical process to produce lead carbonate. The lead carbonate is returned and fed as raw material to the shaft furnace.

### ***Refining and alloying***

The refining and alloying of crude lead is carried out in refining kettles. To alloy the lead, it is remelted and alloying elements are added. Finally it is cast into ingots of approximately 40 kg each. During the refining and alloying of the crude lead, heavy metal emissions arise, for example, depending on the refining process operated. To collect these emissions, primary hoods for dedusting are arranged above the kettles. These are connected to the fabric filter.

### ***Water management/waste water treatment***

A certain amount of water is used for regular wet cleaning of the plant site and vehicles. Wet cleaning of the site is done using a sweeping machine. Also all trucks are cleaned regularly. To close the water circuit, the used cleaning water as well as the rainwater is collected, and treated in an automatic water treatment plant in several chemical and physical cleaning steps. The quality of the cleaned water is monitored continuously. Part of the treated water from the water treatment plant is reused internally, and the remaining water is discharged. An analysis of discharged water is given in Table 3-61.



### 3.2.2.3 Summarised data on outputs and environmental concerns

#### *Emissions into the air*

Table 3-60 shows the main controlled emissions into the air from the shaft furnace plant L5.

**Table 3-60: Typical controlled emissions into the air from the shaft furnace plant L5**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [mg/Nm <sup>3</sup> ]				
		Dust	Pb	Cd	SO <sub>2</sub>	NO <sub>x</sub>
Gas cleaning system	65,000	< 1.0	< 0.5	< 0.05	< 500	< 50

Source: company information company L5, 1998

#### *Waste water*

The only source of water discharges is the central water treatment plant, in which all water like cleaning water and rainwater is treated. Purified water not required internally is discharged. Data on waste water are given in Table 3-61.

**Table 3-61: Typical data on waste water from the shaft furnace plant L5**

Process unit	Effluent [m <sup>3</sup> /a]	Flow [m <sup>3</sup> /h]	Main components [mg/l]					pH
			Pb	Cd	Fe	Zn	Cu	
Waste water treatment plant	17,000	n. a.	< 0.2	< 0.1	< 0.5	< 0.3	< 0.1	6.5 - 8.5

Source: company information company L5, 1998

#### *By-products and residues*

About 95 % of the shaft furnace slag is fed back as return slag to the shaft furnace process, after the iron - lead matte has been separated after solidification [82]. Due to its physical and chemical properties, excess slag is used for road and pathway construction. The iron - lead matte consists primarily of iron, lead and sulphur and is sold to companies in the primary lead making industry for lead and sulphuric acid recovery. The lead dross arising from the refining processes is sold for metal recovery. An overview of the by-products and residues is given in Table 3-62.

**Table 3-62: By-products and residues from the shaft furnace plant L5 (1997)**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Battery treatment	Spent battery acid	3,350	External recycling
Shaft furnace	Slag	1,500	Internal recycling Road construction
	Flue dusts	950	External/internal recycling
	Iron/lead matte	4,200	By-product for sale to primary lead production plants
Refining	Lead dross	3,100	By-product for sale to metal recovery

Source: company information company L5, 1998

### ***Other environmental concerns***

In the vicinity of the plant L5 the dust and lead immissions are monitored according to the German regulations TA Luft (c.f. Annex). Suspended dust collection gives immission values on a annual average basis for lead and inorganic lead compounds of less than 1 µg/Nm<sup>3</sup>. The dust sediment has a content of lead and inorganic lead compounds of less than 0.15 mg/m<sup>2</sup> per day.

### **3.2.3 Lead production from secondary raw material using rotary furnaces**

In Germany, several rotary furnaces are in operation for the processing of secondary raw materials. Among them, two types for the treatment of lead-acid batteries are in use:

- smelting after battery breaking, dismantling and separation into different materials fractions
- smelting of entire batteries after acid drainage.

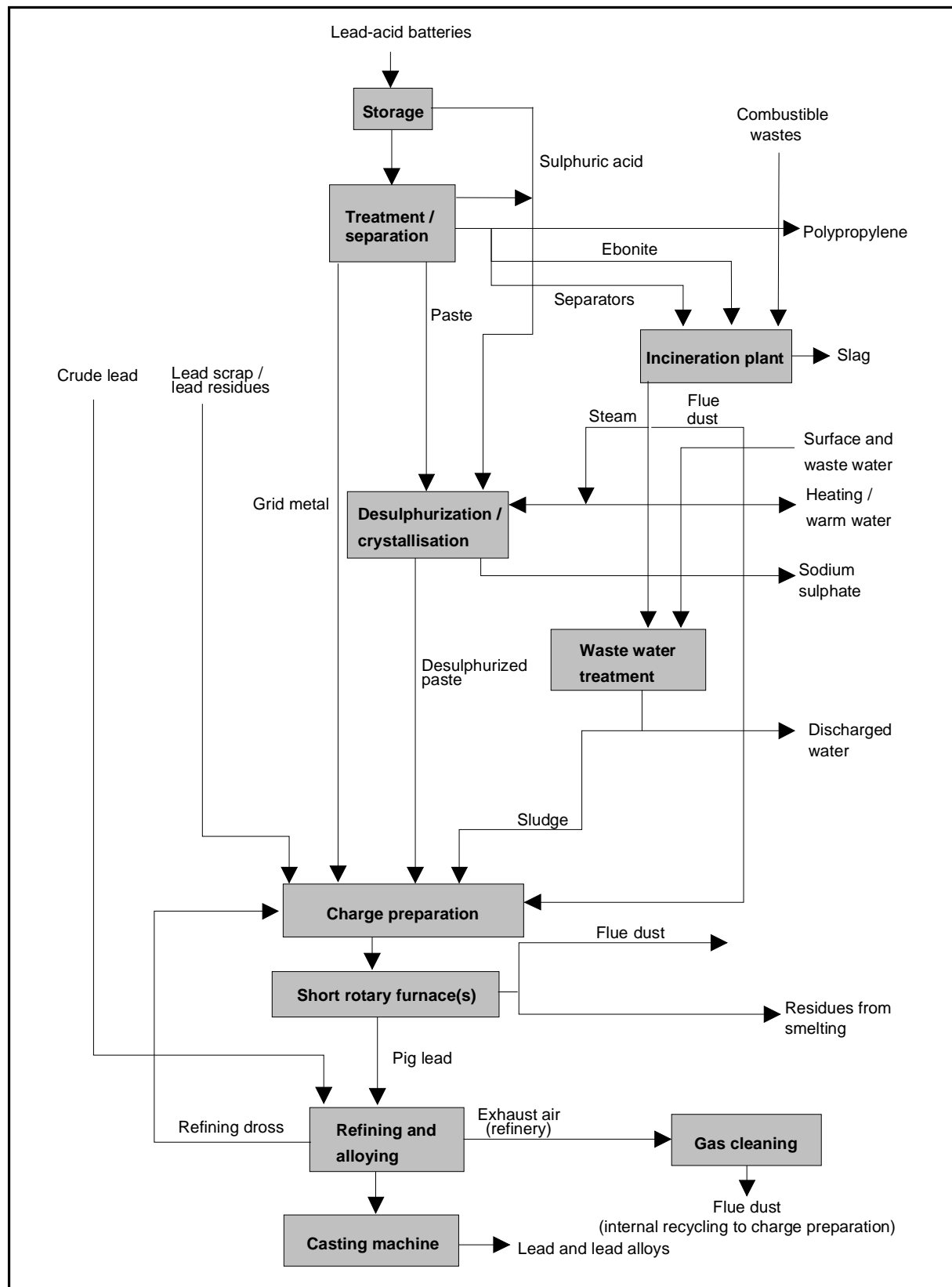
#### **3.2.3.1 Rotary furnace plant L4**

##### **3.2.3.1.1 General information**

Since 1995, company L4 is operating a modern secondary lead production plant. At this location, lead production has a tradition over 600 years. About 40 Million DM have been invested for the modernisation of the old smelting plant. The new recycling process recovers lead from used lead-acid batteries. The process comprises the following main steps:

- treatment and separation of old batteries,
- desulphurization of electrode paste using sodium hydroxide,
- smelting in (two) short rotary furnaces,
- refining and alloying of the lead bullion, and
- incineration plant for hazardous waste.

A schematic view of this process is given in Figure 3-21. A peculiarity of the site L4 is the integration of a modern waste incineration plant with a capacity of 33,000 t/a at the same location. Parts of the incineration plant capacity are used for thermal treatment of the company's own plastic wastes from battery recycling. Additionally special wastes from external sources are processed. The whole plant is certified according to ISO 9001, EMAS and ISO 14001 [6]. An overview of the specific input and output values of the lead recycling plant L4 as well as the waste incineration plant is given in Table 3-63 and Table 3-64.



**Figure 3-21: Lead recycling plant L4**

Source: Behrendt et al. [6]

**Table 3-63: Specific annual input and output values of the lead recycling plant L4 (incl. refinery, 1997)**

Input <sup>*)</sup>			Output <sup>*)</sup>		
<b>Melting materials</b>	[t/t Pb]	1.41	<b>Products</b>		
<i>hereof:</i> battery scrap	[%]	79.0	Lead and lead alloys	[t/t Pb]	1
Other melting materials	[%]	3.8	Sodium sulphate	[t/t Pb]	0.096
Bullion, scrap lead	[%]	16.6	Polypropylene chips	[t/t Pb]	0.051
Flue dust incinerator	[%]	0.6	<b>Wastes</b>		
<b>Reagents</b>	[t/t Pb]	0.307	Residual plastics	[t/t Pb]	0.108
<i>hereof:</i> NaOH	[%]	49.8	Metallurgical slag	[t/t Pb]	0.18
Steel borings	[%]	9.4	<b>Others:</b> Exhaust gases	[Nm <sup>3</sup> /t Pb]	37,000
Petrol coke	[%]	17.6			
Soda	[%]	23.1			
<b>Others:</b> Electric energy	[MWh/t Pb]	0.20			
Natural gas	[MWh/t Pb]	0.73			
Steam	[MWh/t Pb]	0.84			

<sup>\*)</sup> As indicated, all figures are given per ton of lead and lead alloys produced.

Source: company information company L4, 1998

**Table 3-64: Specific annual input and output values of the waste incineration plant (company L4, 1997)**

Input <sup>*)</sup>			Output <sup>*)</sup>		
Residual plastics (own)	[t/t Pb]	0.108	Steam	[MWh/t Pb]	1.033
Other input	[t/t Pb]	0.074	Incinerator slag	[t/t Pb]	0.04
Water	[m <sup>3</sup> /t Pb]	3.15	Flue dust (to lead smelter)	[t/t Pb]	0.009
Electric energy	[MWh/t Pb]	0.029	Waste water	[m <sup>3</sup> /t Pb]	4.3
Natural gas	[MWh/t Pb]	1.087	Exhaust gas	[Nm <sup>3</sup> /t Pb]	2,000

<sup>\*)</sup> As indicated, all figures are given per ton of lead and lead alloys produced.

Source: company information company L4, 1998

### 3.2.3.1.2 Description of the main process units and environmental techniques

In the following, detailed information on the main environmental measures in the different process units is given. Besides technical data, input and output levels are presented, where available.

#### **Raw material handling**

Lead-acid batteries are the main input material, other lead bearing wastes are only processed to a minor extent. First of all, the delivered batteries are stored in an acid-resistant, roofed storage yard. Most of the acid is drained and captured in a pump-sump, then filtered and

collected for the neutralisation of surplus sodium hydroxide from the desulphurization plant. The old batteries are crushed and treated hydrodynamically by screening and separation in order to classify different fractions of polypropylene, ebonite, separators (PE, PVC, glass), metallic grid lead and electrode paste. The electrode paste, which contains sulphur as lead sulphate, is treated hydrometallurgically with sodium hydroxide. The lead sulphate reacts to sodium sulphate, water and lead oxide. The lead oxide is separated by filtering and then smelted.

### ***Rotary furnaces***

For the smelting of raw materials, two short rotary furnaces are operated. Within these, different charges of lead containing substances, mainly metallic grid, returned filter dusts and desulphurised paste are smelted at 1,000°C in order to produce crude lead or partly a lead-antimony alloy for further processing in the refining plant. An automatic charging crane is used for charging the input materials. The furnaces, with a capacity of 5 m<sup>3</sup> each, are totally encapsulated. The crude lead is tapped together with the slag into kettles by tilting the furnace. After a cooling down period, the lead bullion and slag are separated and transferred to the subsequent processing units. Emissions from smelting furnaces, like gaseous and particulate heavy metal emissions, are effectively collected from the waste process gas and passed to the gas cleaning system. The furnaces are totally encapsulated to prevent fugitive emissions from charging as well as from furnace operation.

### ***Gas cleaning system (rotary furnaces)***

The furnace off-gas is cooled down for heat-recovery and steam is generated and used internally e.g. for dewatering or drying. A typical analysis of the clean gas from the smelting furnaces is given in Table 3-65.

**Table 3-65: Typical average analysis of the clean gas from the short rotary furnaces**

Process unit	Main components [mg/Nm <sup>3</sup> ]						PCDD/PCDF [ng-TE/Nm <sup>3</sup> ]
	Dust	Pb	SO <sub>2</sub>	HCl	NO <sub>x</sub>	CO	
Rotary furnaces A+B	0.15 - 0.52	0,04 - 0.1	86	< 5	15 - 20	94 - 108	0.08

Source: company information company L4 [62]

### ***Refining plant***

The lead bullion is transferred to the refining plant. Up to 13 kettles are used for refining and alloying about 35 different qualities of lead and lead alloys. The resulting lead or lead alloys are cast in ingots (about 45 kg each) or blocks (about 1,000 kg each). Chemical reactions taking place during the refining and alloying of the lead give rise to various emissions in the refinery. The emissions depend on the type of refining process operated, whereby mainly heavy metal emissions arise. In order to collect these emissions, primary hoods for dedusting

are arranged above the kettles and connected to a ventilation system. The off-gases are cleaned in fabric filters.

### ***Waste incineration plant***

The waste incineration plant was technically revamped in 1996. The main feature of the new incineration plant is the modern gas cleaning system, which results in a high reduction of emissions. The off-gas from the waste incineration plant fulfils the requirements according to the German regulations 17. BImSchV. According to the operating permit, the maximum capacity for the rotary kiln operation is 33,000 t/a. The flue dust from the incineration plant gas cleaning devices shows a high lead content and is recycled to the rotary furnaces ([6],[7]). Altogether, about 99 % of the lead is recovered in solid products.

### ***Waste water treatment plant***

All water used at the site is purified internally. The process water from battery treatment is recirculated. All the water used (e.g. process water, cleaning water) is collected and treated in the central water treatment plant.

**Table 3-66: Annual average analysis of water discharges from the recycling plant L4**

Element	Pb	Cd	As	Zn	Ni	COD	AOX
[mg/l]	0.15	0.007	0.07	0.42	0.11	43.0	0.23

Source: company information company L4 [62]

### ***3.2.3.1.3 Summarised data on outputs and environmental concerns***

#### ***Emissions into the air***

Table 3-67 shows the main controlled emissions into the air from the lead recycling plant L4.

**Table 3-67: Controlled emissions into the air from the lead recycling plant L4**

Process unit	Flow [Nm <sup>3</sup> /t Pb]	Main components [g/t Pb]				
		Dust	Pb	SO <sub>2</sub>	NO <sub>x</sub>	HCl
Rotary furnaces (A + B), refinery	45,000	31	7	1,070	370	n. a.
Waste incineration plant	2,000	3	1.8	43	396	n. a.

Source: company information company L4, 1998

#### ***Waste water***

The water from the waste water treatment plant is discharged (c.f. Table 3-68). In 1996, 190,000 m<sup>3</sup> water were discharged. Sludges from filtering are dewatered in a filter press and

recycled to the smelting furnaces. In Table 3-68, data on the waste water which include surface waters is summarised.

**Table 3-68: Data on waste water from the lead recycling plant L4**

Process unit	Effluent [m <sup>3</sup> /a]	Flow [m <sup>3</sup> /t Pb]	Main components [g/t Pb]						
			Pb	Cd	As	Zn	Ni	COD	AOX
Waste water treatment plant	190,000	4.3	1.4	0.09	0.5	1.6	0.7	225	0.4

Source: company L4 [62]

### ***By-products and residues***

As mentioned above, the recovered sodium sulphate solution is crystallised, dried and sold as chemically pure sodium sulphate salt with less than 5 ppm lead. About 85 % of the sulphur is recovered this way. The polypropylene chips are recompounded in a recovering plant belonging to the subsidiary of the company L4. The produced high quality polypropylene granules are sold. A polypropylene recovery rate of more than 90 % is achieved. Plastic waste and other materials like ebonite that cannot be recycled are burnt in the incineration plant. Only process slag, that cannot be prevented or recycled has to be dumped. An overview of the by-products and residues is given in Table 3-69.

**Table 3-69: By-products and residues from the lead recycling plant L4**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Crystallisation plant	Sodium sulphate	4,300	By-product for sale
Battery treatment	PP granules	2,300	By-product for sale
	Residual plastics	4,900	Waste incineration plant
	Slag	8,100	Recycling, dumping
Short rotary furnaces	Flue dusts	n. a.	Internal recycling

Source: company information company L4, 1998

### ***Other environmental concerns***

Noise emissions have been reduced during recent years, e.g. by the encapsulation of main noise sources like ventilators.



### 3.2.3.2 Rotary furnace plant L6

#### 3.2.3.2.1 General information

Since 1977, the company L6 has operated a secondary lead production plant. At this location, the lead production has a long tradition. A schematic view of the battery recycling process developed and operated by company L6 is given in Figure 3-22. The process plant L6 comprises the main steps [9]:

- treatment and separation of old batteries,
- sale of sulphur-containing electrode paste or desulphurization with sodium hydroxide,
- smelting in short rotary furnaces, and
- refining and alloying of lead bullion.

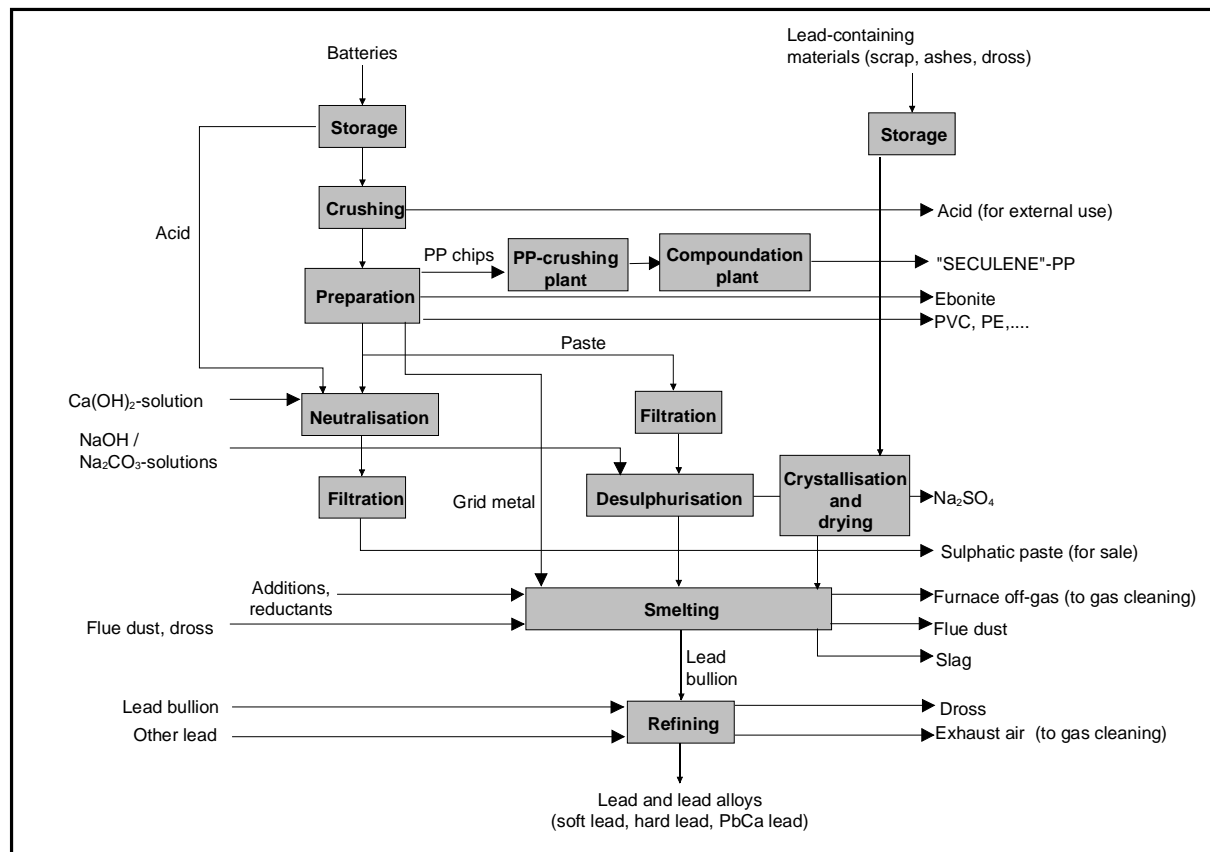
The process has several similarities with the lead recycling plant L4. A peculiarity of this site is the integration of the compoundation plant for polypropylene recovery since 1991. The whole plant is certified according to ISO 9001 and ISO 14001. An overview of input and output materials is given in Table 3-70.

**Table 3-70: Specific annual input and output values of the recycling plant L6 (incl. refinery, 1997)**

Input <sup>*)</sup>			Output <sup>*)</sup>		
<b>Melting materials</b>	[t/t Pb]	2.12	<b>Products</b>		
<i>hereof:</i> battery scrap	[%]	63	Lead and lead alloys	[t/t Pb]	1
Other melting materials	[%]	21	Battery paste	[t/t Pb]	0.5
Bullion, scrap lead	[%]	16	Polypropylene compounds	[t/t Pb]	0.14
<b>Reagents</b>	[t/t Pb]	0.14	<b>Wastes</b>		
<i>hereof:</i> Steel borings	[%]	46	Residual plastics	[t/t Pb]	0.035
Petrol coke	[%]	32	Slag	[t/t Pb]	0.23
Soda	[%]	22	<b>Others</b> Exhaust gases	[Nm <sup>3</sup> /t Pb]	n. a.
<b>Others:</b> Electric energy	[MWh/t Pb]	0.26			
Natural gas	[MWh/t Pb]	1.19			
PP chips (external)	[t/t Pb]	0.04			

<sup>\*)</sup> As indicated, all figures are given per ton of lead and lead alloys produced.

Source: company information company L6, 1998



**Figure 3-22: Process plant L6 for the recycling of used lead-acid batteries**

Source: company information company L6, 1998

### 3.2.3.2.2 Description of the main process units and environmental techniques

In the following, detailed information on the main environmental measures in the different process units is given. Besides technical data, input and output levels are presented, where available.

#### **Raw material handling**

Lead-acid batteries are the main input materials. The delivered batteries are unloaded into an acid-resistant, roofed storage facility. Most of the acid with a sulphuric acid content of 8 - 15 % is drained and captured in a pump-sump for further use in the process. The batteries are crushed using a hammer crusher. By sieving the fine fraction, mainly lead paste, is separated for sale or for further internal processing. For desulphurization, the recovered lead paste is processed with caustic lye of soda or soda. The lead sulphate reacts to sodium sulphate, water and lead oxide or lead carbonate. The coarse fraction is treated hydrodynamically to classify polypropylene, a plastic fraction, and grid metal, which is used for the production of lead bullion alloyed with antimony.

Waste acid is either sold as such as a neutralisation agent in the desulphurisation process or is neutralised with lime and processed with the sulphur containing paste.

### ***Rotary furnaces***

For the production of crude lead, four short rotary furnaces with a capacity of 3.8 m<sup>3</sup> each are operated. At temperatures of up to 1,200°C metallic grid, paste and other lead-bearing compounds are smelted. The heat is supplied by oxygen/natural gas burners. The off-gas produced in the rotary furnaces passes to the gas cleaning system. The molten lead bullion and the slag are separately tapped into moulds. The furnaces are encapsulated to prevent fugitive emissions. The desulphurized paste can also be processed in the rotary furnace. For this purpose, together with the paste, coke and fluxes are charged and lead bullion with a low antimony content is obtained. By processing of different mixtures of raw materials, the content of antimony in the lead bullion can be varied.

### ***Gas cleaning system***

A fabric filter is used to reduce the dust emissions from the rotary furnaces, average emission values are indicated in Table 3-71. A specific off-gas amount of about 65,000 Nm<sup>3</sup>/h arise. After thermal granulation, the flue dust is precipitated and recycled to the smelting furnace.

**Table 3-71: Typical average off-gas values (rotary furnaces)**

Process unit	Main components [mg/Nm <sup>3</sup> ]							PCDD/PCDF
	Dust	Pb	Cd	As	SO <sub>2</sub>	HCl	NO <sub>x</sub>	[ng-TE/Nm <sup>3</sup> ]
Rotary furnaces	< 1 - 10	0.2 - 1	0.001 - 0.01	0.002 - 0.02	< 200	5 - 20	20 - 50	< 0.1 - 1

Source: company information company L6, 1998

### ***Refining and alloying***

At plant L6 site, up to 10 kettles can be used for the refining and alloying of different lead and lead alloy qualities. The product is cast into ingots (about 50 kg each). Because of ongoing chemical reactions, various amounts of emissions arise in the refinery e.g. heavy metals depending on the refining process operated. For collecting these emissions, primary hoods connected to fabric filters are arranged above the kettles.

### ***Compoundation plant***

The polypropylene fraction, recovered by the treatment of batteries in the separation plant, is processed in the compoundation plant. The ground polypropylene chips are compounded, and the manufactured product "Seculene®" can be used for different options, for example in the car manufacturing industry.

### ***Water management/waste water treatment***

The process water for the hydros separation of battery scrap is used in cycles. All waters (e.g. process waters, cleaning water) are collected and treated in the central water treatment plant. The clean water from the water treatment plant is partly used internally. Sludges from filtering are dewatered in a filter press and recycled to the smelting furnaces.

#### ***3.2.3.2.3 Summarised data on outputs and environmental concerns***

### ***Emissions into the air***

Table 3-72 shows the main controlled emissions into the air from the lead recycling plant L6.

**Table 3-72: Controlled emissions into the air from the lead recycling plant L6**

Process unit	Flow [Nm <sup>3</sup> /t Pb]	Main components [g/t Pb]					
		Dust	Pb	Cd	SO <sub>2</sub>	NO <sub>x</sub>	HCl
Rotary furnaces (1 - 4)	9,600	< 10 - 100	2 - 10	0.001 - 0.01	< 2,000	200 - 500	50 - 200
Exhaust air (furnace area, refinery, ...)	21,000	2.1 - 69	0.2 - 2	0.4 - 8	< 440	n. a.	10 - 20

Source: company information company L6, 1998

### ***Waste water***

All waters (e.g. process waters, cleaning water) are collected and treated in the central water treatment plant. The clean water from the water treatment plant is partly used internally. In Table 3-73, data on discharged waste water are summarised.

**Table 3-73: Data on waste water from the lead recycling plant L6 (annual average values)**

Process unit	Effluent [m <sup>3</sup> /a]	Flow [m <sup>3</sup> /h]	Main components [mg/l]						
			Pb	Cd	As	Zn	Ni	COD	AOX
Waste water treatment plant <sup>1)</sup>	110,000	12.7	0.12	0.06	0.05	0.14	0.1	13	0.52

<sup>1)</sup>: no production specific waste waters, only surface water

Source: company information company L6, 1998

### ***By-products and residues***

The by-products and residues are shown in Table 3-74. The sodium sulphate solution is crystallised, dried and sold as chemically pure sodium sulphate salt to the glass or chemical industries. Process slag from the smelting furnaces, that can not be prevented or recycled is dumped.

**Table 3-74: By-products and residues from the lead recycling plant L6**

Process unit	By-product/residue	Amount [t/a]	Use/treatment option
Compoundation plant	PP compounds	4,800	By-product for sale
Battery treatment	Sulphatic paste	17,000	Sale to primary lead production plants
	Residual plastics	1,200	Dumping
Short rotary furnace	Slag	7,800	Recycling, dumping
	Flue dusts	n. a.	Internal recycling

Source: company information company L6, 1998

### 3.2.3.3 Rotary furnace plant L7

#### 3.2.3.3.1 General information

Facing a tradition of more than 450 years of lead processing, the company L7 operates a secondary lead smelting plant since 1971. The main source are spent lead-acid batteries ([56], [57]). The plant comprises the following main steps:

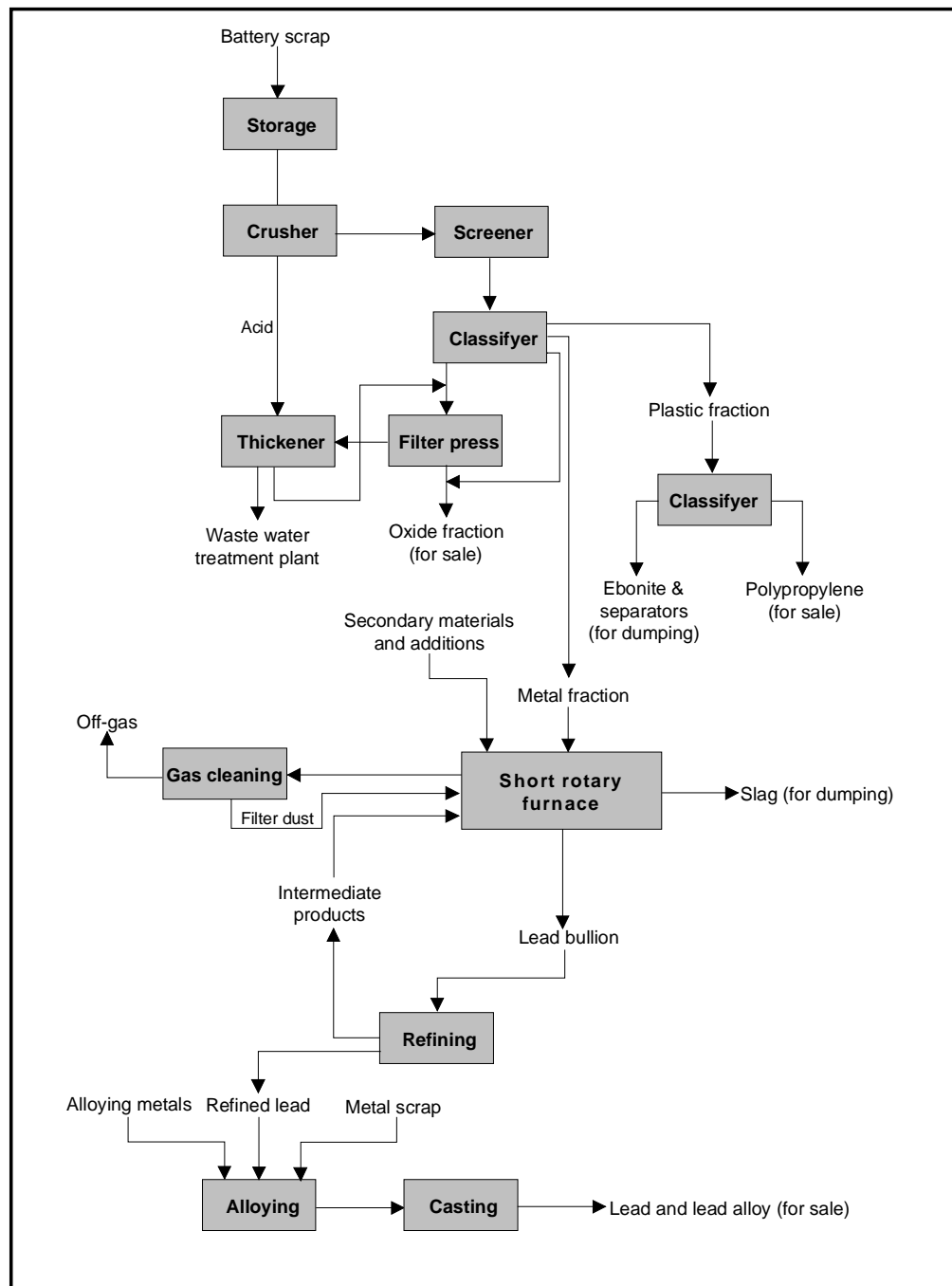
- battery treatment including waste water treatment and polypropylene upgrading,
- smelting in a short rotary furnace,
- refining plant (certified according to DIN ISO 9002).

A schematic view of the lead recycling plant is given in Figure 3-23. The main capacity figures are given in Table 3-75.

**Table 3-75: Main input and output capacity figures of plant L7**

Input	[t/a]	Output	[t/a]
Battery scrap	65,000	Refined lead and alloys	28,000
Battery plates	4,000	Battery paste	32,500
Scrap lead	6,000	PP fine grains	2,750
		Ebonite and separators	3,500
		Slag	3,300

Source: company information company L7, 1998



**Figure 3-23: Lead recycling plant L7**

### 3.2.3.3.2 Description of the main process units and environmental techniques

In the following, detailed information on the main environmental measures in the different process units is given. Besides technical data, input and output levels are presented, where available.

### ***Raw materials***

The delivered batteries are stored in an acid resistant partly roofed storage area. The free acid is drained and directed to the waste water treatment installation. The batteries are crushed and separated in a battery treatment plant. Four different fractions are produced:

- the metal fraction consisting of poles, connectors and grids,
- battery paste to be shipped to a primary lead production plant,
- polypropylene chips for further treatment in the upgrading installation (washing and cutting plus air-blowing), and
- the separator and ebonite fraction for disposal.

### ***Rotary furnace***

For the smelting of the lead containing materials, mainly the metal fraction from the battery treatment plant, but also drosses from the refinery and internal filter dusts, a short rotary furnace is used. The produced lead bullion is tapped into iron pots and transferred to the refinery. The slag produced in the rotary furnace is silica based and gives very low eluate values for lead. Therefore, the slag must not be dumped as hazardous waste.

### ***Gas cleaning system***

By mixing with ventilation air, the furnace off-gas is cooled. For dedusting a bag filter (specific dust load: 0.7 m<sup>3</sup>/m<sup>2</sup>h) is used. The filter dust is wetted and returned back to the rotary furnace. A typical clean gas analysis is given in Table 3-76.

**Table 3-76: Typical analysis of the clean gas from the rotary furnace (plant L7)**

Process unit	Main components [mg/Nm <sup>3</sup> ]					PCDD/PCDF [ng-TE/Nm <sup>3</sup> ]
	Dust	Pb	SO <sub>2</sub>	HCl	NO <sub>x</sub>	
Rotary furnace gas cleaning	2	0.8	220	n. a.	20	< 0.1

Source: company information company L7, 1998

### ***Refining plant***

The lead bullion is refined in up to 11 kettles with a capacity of 100 tons each. In order to meet customers' specifications, about 40 different lead alloys are produced. Most of the lead produced is used by battery manufacturers.

To collect the emissions from the kettles, a ventilation system with dedusting hoods is arranged above the kettles. The ventilation air is cleaned in a bag filter.

### 3.2.3.3.3 Summarised data on outputs and environmental concerns

#### Emissions into the air

Table 3-77 shows the main controlled emissions into the air from the lead recycling plant L7.

**Table 3-77: Controlled emissions into the air from the lead smelting plant L7**

Process unit	Flow [Nm <sup>3</sup> /h]	Main components [mg/Nm <sup>3</sup> ]			
		Dust	Pb	NO <sub>x</sub>	SO <sub>2</sub>
Rotary furnace and refining plant	126,000	1.8	0.4	15	105

Source: company information company L7, 1998

#### Waste water

The water from the waste water treatment plant is discharged, a typical analysis is given in Table 3-78.

**Table 3-78: Data on waste water discharged from the lead smelting plant L7**

Process unit	Effluent [m <sup>3</sup> /a]	Flow [m <sup>3</sup> /h]	Main components [mg/l]						
			Pb	Cd	As	Zn	Ni	COD	AOX
Waste water treatment plant	124,000	n. a.	0.02	0.07	< 0.001	0.27	0.09	n. a.	0.2

Source: company information company L7, 1998

#### By-products and residues

The fraction of separators and ebonite from the battery treatment plant and the slag from the short rotary furnace are dumped on an own dump at the plant site. Sludges from the water treatment plant contain the gypsum from the neutralisation of sulphuric acid and are sold as a part of the battery paste to a primary lead production plant.

### 3.2.3.4 Rotary furnace plant L8

#### 3.2.3.4.1 General information

Since 1960, the company L8 has operated a lead recycling plant.<sup>20</sup> In 1992, several modernisation projects were realised to improve productivity and environmental performance. The plant comprises the following main steps:

- raw material handling,
- smelting in short rotary furnaces, and
- refining and alloying of lead bullion.

<sup>20</sup> The information supplied in this chapter is mainly based on information given by the company L8 in 1998.



An overview of input and output values is given in Table 3-79.

**Table 3-79: Input and output values of the lead recycling plant L8**

Input	[t/a]	Output	[t/a]
Lead-containing materials	12,000	Lead bullion	10,000
Sodium carbonate	920	Dross	2,100
Coal	290	Lead-containing flue dust	240
Fuel oil	828	Slag	2,000
Oxygen	2 10 <sup>6</sup> m <sup>3</sup>	Loaded adsorbent	87
Loaded adsorbent	87		
Limestone additive	40		
Lead containing flue dust	240		
Antimony, antimony alloys	370		
Pyrit	73		

Source: company information company L8

#### 3.2.3.4.2 Description of the main process units and environmental techniques

##### *Raw materials*

For raw material, mainly used lead-acid batteries and residues from the lead-acid battery production are taken. In addition, several lead containing fractions are recycled internally, like filter dusts and sludges from the waste water treatment. The main other input materials are sodium carbonate, coal and to a smaller extent iron containing additives. After drainage, complete lead-acid batteries are charged without further preparation.

##### *Rotary furnace*

A wheel loader is used for handling of raw materials. The furnace is charged via a charging wagon with a capacity of 4 - 5 tons of raw materials. Emissions from the charging area are captured by hoods. For each furnace charge, the charging wagon has to be loaded and unloaded into the furnace five to ten times. This frequency is determined by the composition of the input materials, e.g. the content of plastic material. The new wagon charge is not unloaded into the furnace until the plastic material from the last charge has burnt down. After the final wagon charge, the furnace is closed hydraulically.

The tiltable furnace has a capacity of 25 tons, and a lead bullion production of about 18.6 tons per charge or 55 tons per day is achieved. For smelting the input charge, heat is supplied by an oil oxygen burner at the back of the furnace. Thus a considerable reduction of the energy consumption as well as the amount of the off-gas is realised. During the charging phase, the furnace off-gas amounts to about 5,000 Nm<sup>3</sup>/h. In the subsequent reduction phase, only 1,000 Nm<sup>3</sup>/h are exhausted. After the reduction is finished, the slag is tapped into the slag moulds. Afterwards the lead bullion is tapped into the lead moulds and transferred to the

refining and alloying vessels. Due to its composition with a high content of water soluble sodium salts and heavy metal compounds, the slag has to be deposited.

### ***Refining and alloying***

For refining and alloying, two oil and gas heated vessels with a capacity of 30 tons each are used. The emissions of the refining and alloying vessels are collected by hoods. The exhaust gas (up to 4,000 Nm<sup>3</sup>/h) is ventilated to the gas cleaning system, where a cyclone is used as the first cleaning device (c.f. Figure 3-24). Drosses are separated from the vessels with an automatic separation device.

### ***Gas cleaning system***

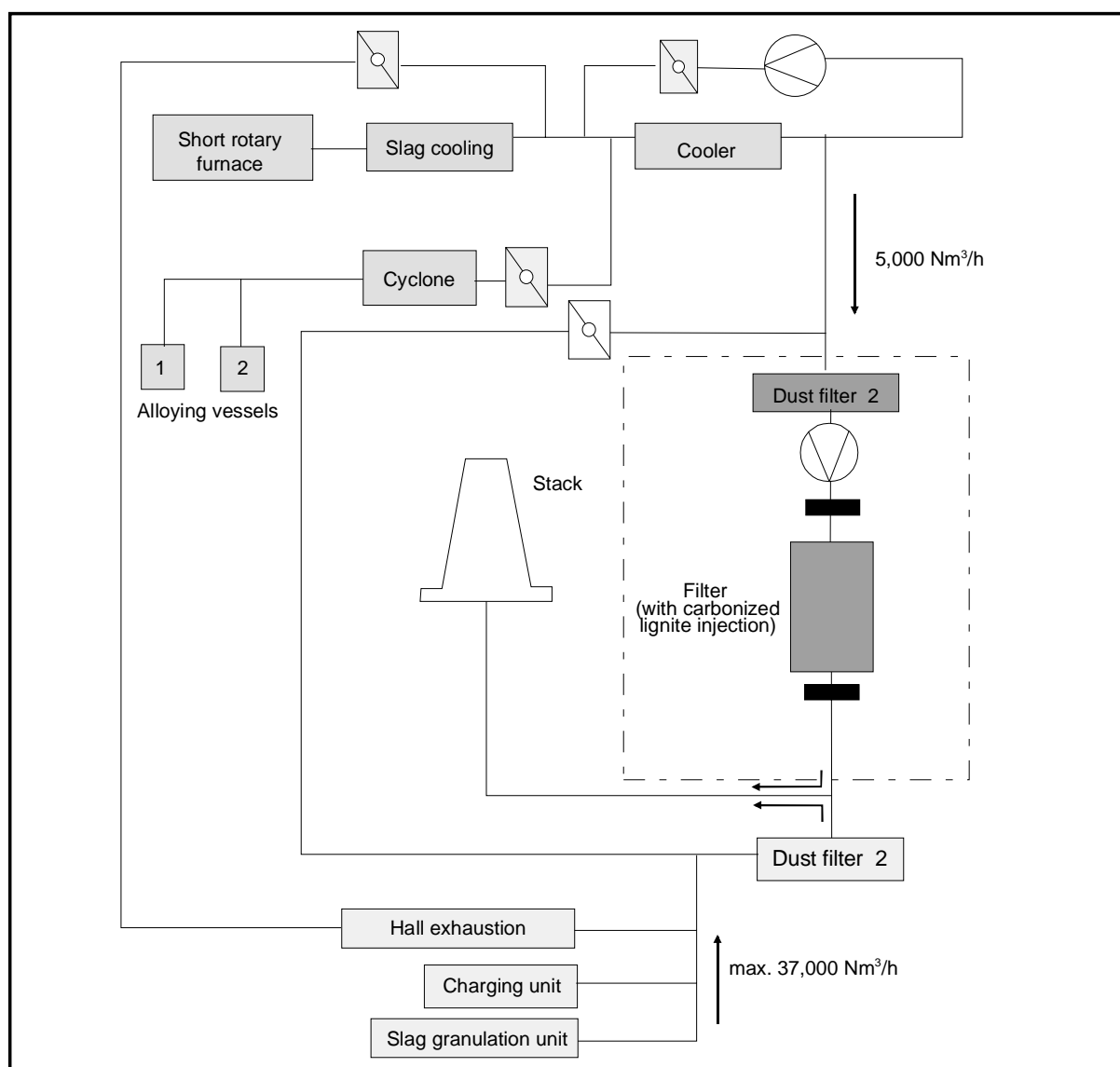
A schematic view of the gas cleaning system is given in Figure 3-24. In the slag chamber, the hot off-gas with a temperature of about 1,200°C is cooled down to 250°C by mixing it with circulating air. After cooling down to a temperature of less than 120°C in a second cooler, the off-gases from the rotary furnace and the refining plant are cleaned in a two stage gas cleaning system. First a fabric filter with a filter area of about 160 m<sup>2</sup> is used. The precipitated dust from the two fabric filters is granulated by the addition of water and the dust pellets are re-processed into the furnace. For final purification, the pre-dusted off-gases are passed to an adsorption filter, where activated carbonised lignite is used as adsorbent. This filter consists of six parallel adsorbent boxes and permits the precipitation of vaporous and solid substances, like sulphur dioxide, heavy metal compounds and organic compounds. The loaded lignite is discharged from the boxes and used as a reduction agent in the rotary furnace. The clean gas composition given in Table 3-80 has been derived from sample measurements.

**Table 3-80: Composition of the clean gas from the short rotary furnace (plant L8)**

Process unit	Main components [mg/Nm <sup>3</sup> ]					PCDD/PCDF [ng-TE/Nm <sup>3</sup> ]
	Dust	Pb	SO <sub>2</sub>	HCl	NO <sub>x</sub>	
Rotary furnace gas cleaning	5 - 10	0.08 - 0.15	30 - 50	7 - 9	200 - 400	< 0.1

Source: company information company L8, 1998

If unusually high sulphur dioxide concentrations in the off-gas occur e.g. during the charging phase or the processing of loaded adsorbent, the injection of limestone additive and water after the cooling steps is foreseen.



**Figure 3-24: Modernised gas cleaning system of plant L8**

### 3.2.3.4.3 Summarised data on outputs and environmental concerns

#### Emissions into the air

Table 3-81 shows the main controlled emissions into the air from the lead recycling plant L8.

**Table 3-81: Controlled emissions into the air from the lead recycling plant L8**

Process unit	Flow [Nm³/h]	Main components [mg/Nm³]			
		Dust	Pb	Cd	SO <sub>2</sub>
Rotary furnace gas cleaning	n. a.	5 - 10	0.08 - 0.15	n. a.	30 - 50

Source: company information company L8, 1998

### ***Waste water***

The waste water from the plant L8 is treated in the central waste water treatment plant of the neighboured lead batteries manufacturing plant. In Table 3-82, the permitted concentration limit values for clean water discharged from the waste water treatment plant are given. The regularly monitoring of the waste water treatment plant show, that the measured clean water concentrations are lower than the limit values.

**Table 3-82: Data on waste water discharged from the company L8**

Process unit	Effluent [m <sup>3</sup> /a]	Flow [m <sup>3</sup> /h]	Main components [mg/l]						
			Pb	Cd	As	Zn	Ni	COD	AOX
Waste water treatment plant	150,000	40	0.4	0.01	< 0.001	0.01	< 0.05	96	0.25

Source: company information company L8, 1998

### ***By-products and residues***

An annual quantity of 2,000 tons of furnace slag has to be deposited. The other solid outputs from the different processing units, mainly filter dusts, loaded adsorbent and lead dross, are recycled internally.

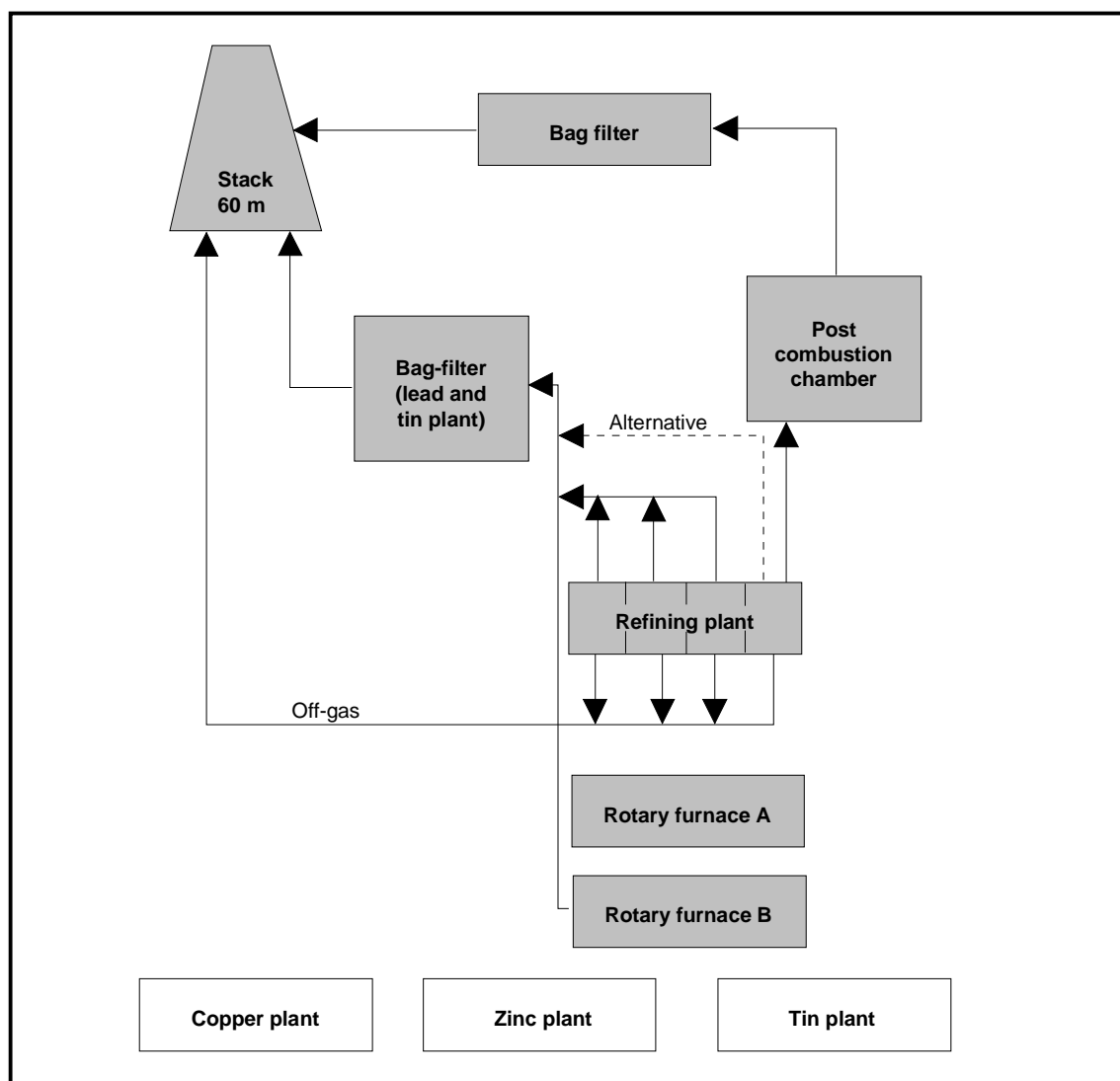
#### **3.2.3.5 Rotary furnace plant L9**

At the lead recycling plant L9 about 15,000 tons of lead bullion are produced per year from lead scrap and used lead-acid batteries. Lead scrap is processed together with drained batteries and fluxes in a short rotary furnace. The main products are lead-antimony alloy, used sulphuric acid, lead-iron matte, slag, and dust.

- No further information available -

### 3.2.3.6 Rotary furnace plant L10

At the lead recycling plant L10, a short rotary furnace is used for the production of lead mainly from scrap and spent batteries. In addition, secondary copper, zinc, and tin are produced at the plant site. A schematic view of this plant is given in Figure 3-25.



**Figure 3-25: Lead recycling plant L10**

- No further information available -



## 4 German candidate best available techniques for integrated pollution prevention and control in the zinc and lead production

In this chapter, German *candidates best available techniques* (CBAT) will be described as a basis for the later determination of BAT on an EU level. For the identification of German CBAT, the IPPC-Directive, that is to say the definition of BAT in Art. 2.11 IPPC-D, serves as a basis:

"Best available techniques" shall mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole: Techniques shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned, Available techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator. Best shall mean most-effective in achieving a high general level of protection of the environment as a whole." According to the IPPC-Directive, in the identification of BAT special consideration should be given to the following items listed in Annex IV:

- "the use of low-waste technology",
- "the use of less hazardous substances",
- "the furthering of recovery and recycling of substances generated and used in the process and of waste, where appropriate",
- "comparable processes, facilities or methods of operation which have been tried with success on an industrial scale",
- "the nature, effects and volume of the emissions concerned",
- "the commissioning dates for new or existing installations",
- "the consumption and nature of raw materials (including water) used in the process and their energy efficiency",
- "the need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risk to it", and
- "the need to prevent accidents and to minimise the consequences for the environment".

First, general aspects and requirements valid for the production of zinc and lead in Germany are summarised (c.f. Chapter 4.1). Taken the information about the German plants and applied techniques (c.f. Chapter 2 and 3) into account, in the Sections 4.2 (zinc production) and 4.3

(lead production), *individual techniques* (which are considered to be "best available"-candidates) for each of the relevant production routes are presented. The *achieved emission and emission load levels*, given for each of the main production routes, have been reached with the processes in combination with the environmental measures. Since this report deals only with the processes and techniques operated in Germany, the derived German CBAT presents the situation in Germany. Other combinations of processes and environmental measures in operation within Europe have not been investigated.

#### **4.1 General provisions and requirements for the prevention and control of environmental pollution**

In the following sections general measures are presented, which can be applied to prevent and control emissions into the atmosphere as well as discharges of waste water and to prevent the formation of solid wastes. In addition measures and general rules for other areas of environmental concerns as noise, plant safety and energy use are described. Only a short overview will be given, detailed technical information can be found elsewhere e.g. in Oslo and Paris Commission [65] and Zierock [114].

##### **4.1.1 Techniques to prevent and control emissions into the atmosphere**

Emissions into the atmosphere can be subdivided into fugitive and controlled (or stack) emissions. Controlled emissions are all captured emissions, which can usually be treated with appropriate gas cleaning devices. Sources for fugitive emissions are roofs and openings of production buildings as well as inadequate enclosed transport system and leakages. They also can arise during open handling and storing of materials. An overview on the relevant emissions and emissions sources in zinc and lead production plants has already been given in Chapter 2.

In order to prevent and control emissions into the atmosphere, different so-called primary and secondary measures can be applied. Since most of the primary measures that prevent the formation of contaminants during the production process, are mainly process specific, they are discussed in the later Chapters 4.2 or 4.3.

###### **4.1.1.1 Measures for the prevention of fugitive emissions**

The contribution of fugitive emissions to the total emissions from a plant site can be very significant and, if appropriate cleaning of the captured gases is applied, exceed in most cases the controlled (stack) emissions. In the following, general measures to prevent and to capture fugitive emissions from storage, handling and transfer operations of dusty materials and from the operation of production and recycling units are summarised. It should be mentioned, that, as a rule, these measures are wide-spread although their realisation strongly depends on the site-specific constraints.



***Storage, handling and transfer operations of dusty materials***

During storing, handling and transfer of materials consisting of fine particles such as concentrates, drosses and filter dusts, emissions of particulate matter can occur. When these dusty materials are stored, the following measures can help to reduce fugitive emissions:

- roofing and complete side coverage for bulk good storage including secondary facilities,
- capturing of exhaust air and adequate cleaning (c.f. Section 4.1.1.2),
- storage in closed container (protection against wind-blown emissions),
- coverage of the surface, e.g. with mats,
- planting of green belt to protect against wind erosion,
- establishing overgrown earth embankment, windbreak plantings or windbreak hedges,
- achieve and maintain a sufficient surface moisture level, i.e. with sprinkler.

In order to prevent fugitive emissions from the handling of dusty materials, the following measures can be applied:

- delivery of raw materials in non-dusting form (wetted, pelletized, briquetted) or in packed form (drums, bins, Big-bags, containers, etc.) Raw materials can be received wetted as far as the process technology is suited for the processing of an additional water input,
- complete enclosure of the machinery, equipment and other facilities used for the treatment or production of dusty goods, and
- installation of exhausters and dedusting devices at main emission relevant parts, i.e. stationary reception, transfer and discharge points of concentrates, shovel loaders and transport units, downspout of loading facilities.

When dusty materials are transported, the following measures can prevent fugitive emissions:

- careful on-site traffic management is required (e.g. minimisation of transport events, restriction for vehicles to designated ways, functions and areas),
- reduced speed for vehicles at the plant site,
- roads should be well defined, well maintained, kerbed, cambered and gullyed to obtain a maximum run-off and collection of water,
- roads should be kept wet after cleaning when appropriate,
- regular cleaning of access roads with cleaning machines,
- reduction of vehicle contact with the stockpile,
- usage of adequate in-plant transport facilities, like pneumatic transport systems or special equipped conveyor systems with ventilation to a filter system, and
- careful cleaning of vehicles, especially their wheels, before leaving plant site.

***Operation of production and recycling units***

In order to prevent fugitive emissions during the operation of production and recycling units, devices for the extraction of process gases should be applied at emissions sources such as furnaces, launders, melting pots, crushers for recycling material, etc. The extraction volumes

of these devices should be sufficient to cope also with abnormal operation conditions and overloads. The captured off-gases should be adequately cleaned (c.f. Section 4.1.1.2). Encapsulating measures can include:

- enhousing of furnaces,
- lock chambers on charging systems,
- close hooding at tapping points,
- dog-house for ladles during tapping,
- enclosure of hot dressing areas, and
- arrestment devices for crushers.

To prevent emissions of particulate matter in the working area, high capacity vacuum cleaning systems should be used for cleaning and maintenance works. For storing, handling and transport of materials containing higher concentrations of lead, cadmium, or other harmful substances, the most efficient measures should be taken.

#### **4.1.1.2 Techniques for the treatment of controlled emissions**

Depending on their physical state, contaminants contained in the gas streams can be classified into gases, vapours and particulate matter. For removal of these contaminants from the gas streams (process gas, exhaust air), different gas cleaning devices are available as shown in the examples in Table 4-1. Normally dry off-gas cleaning is applied. But for certain cases, for example if gaseous compounds or vapours such as mercury vapour have to be precipitated, may additional wet gas cleaning be necessary. Wet gas cleaning is also applied for the cleaning of off-gases with a very high humidity. When choosing a gas cleaning device, in each specific case the following criteria have to be considered:

- process and operation characteristics,
- raw gas characteristic: temperature, humidity, composition, flow, etc.,
- dust characteristic: mass flow, grain size distribution, etc.,
- space requirements,
- separation efficiency, clean dust content, and
- operation safety, capital expenditure and operation costs

As an example, different gas cleaning techniques to remove certain gaseous contaminants and vapours are shown in Table 4-2. The double function of sulphuric acid plants used in the zinc and lead production plants is the removal of sulphur dioxide from the off-gas and the recovery of sulphuric acid as an by-product (c.f. Table 4-2).

**Table 4-1: Different gas cleaning devices (examples)**

Removal of ...	Gas cleaning device	Remark/example	Reference
Particulate matter	Settling chambers	-	-
	Cyclones	Used as pre-precipitator device	VDI 3676 [104]
	Electrostatic precipitators - Dry - Wet	- Dedusting of SO <sub>2</sub> -containing off-gases (dry/wet ESP) - off-gas from slag granulation (wet ESP)	VDI 3678 [106]
	Scrubber (wet separators for particle collection)	Removal of SO <sub>2</sub> , acid mists, ... Use of water requires water treatment and corrosion control in most cases	VDI 3679 [107]
	Fabric filter (filtering separators)	Fabric filters are the most used filtering system. Adequate filter materials have to be selected (elevated temperatures)	VDI 3677 [105]
Gaseous contaminants and vapours	Absorption into a liquid using packed, plate or spray towers	Boliden/Norzink process for the removal of mercury	VDI 3679 [108]
	Adsorption on a solid in a fixed bed	Lead sulphide process for the removal of mercury	VDI 3674 [103]
	Chemical conversion using a catalytic reactor	-	VDI 3476 [101]

**Table 4-2: Techniques to remove gaseous contaminants (examples)**

Substance to remove	Process	Remarks
Sulphur dioxide	Recovery of sulphuric acid in - Single contact plant - <b>Double contact plant</b> <sup>1)</sup> - Wet catalysis - Processes based on NO <sub>x</sub>	- minimum SO <sub>2</sub> concentration necessary - steady off-gas conditions necessary
	Recovery as liquid sulphur dioxides by - Condensation processes - Absorption processes	-
	Recovery as elemental sulphur	-
	Dry sorption of SO <sub>2</sub> by calcium oxide	SO <sub>2</sub> concentration too low for contact acid plant, unsteady conditions
Mercury vapour	Wet absorption processes: - Selenium filter - <b>Boliden/Norzink process</b> <sup>1)</sup> - <b>Sodium sulphate process</b> <sup>1)</sup>	- subsequent sulphuric acid recovery
	Dry adsorption processes: - Activated carbon filter - Lead sulphide process	-
Carbon monoxide and volatile organic compounds	<b>Post-combustion (afterburning) chamber</b> <sup>1)</sup>	-

<sup>1)</sup>: Among others, these techniques are applied in the German zinc and lead production plants.

Source: according to Osparcom [65]

#### **4.1.2 Techniques for the reduction of water consumption and the control and treatment of waste water (water management)**

The sources and the composition of waste water discharged from zinc and lead production plants have been summarised in Chapter 2 and 3. As shown, the main liquid effluent arising in zinc and lead production are from cooling, slag granulation, surface run off and wet gas cleaning operations. In the following, general techniques for the prevention of uncontrolled discharges, the reduction of water consumption and the volume of waste water, and the end of pipe treatment of waste water are summarised. It has to be mentioned, that the waste water situation in non-ferrous metal production plants is strongly determined by site specific conditions [94]. Main location dependent factors are the availability of water, especially for cooling purposes and the existence of a communal waste water system and the possibility to use a public sewage water system after pre-treatment of the effluents.

In general, measures in order to prevent uncontrolled discharges due to leakages or accidents are necessary. These measures should include facilities to contain process waters, site drainage waters, emergency fire water and chemically contaminated waters. Bunding of storage tanks or double walls for tanks are essential in many cases, where there is a risk to controlled waters, sewers and drains, and on-site effluent treatment plants. Shared bunds are possible in cases where the materials stored are not incompatible. Depending on the specific potential for water pollution of the substances, different retention capacities have to be foreseen. High level alarms and trips on storage tanks should be designed according to the requirements. These devices as well as bunds should be inspected on a regular basis, especially where corrosive substances are involved.

To reduce the water consumption and the volume of waste water process integrated measures, such as recycling and reuse are applied. End of pipe treatment is necessary in order to control the pollutant load of the effluents. In order to prevent uncontrolled discharges that may arise due to leakages or accidents safety of devices such as collecting basins are used. For the prevention of accidents and the minimisation of their consequences, several safety measures have to be applied (c.f. Section 4.1.6). Waste water systems have to be monitored and maintained on a regularly basis, especially systems which are installed underground.

##### ***Process integrated measures***

The most important process integrated measures in order to limit the volume of liquid effluents are based upon *recycling* and/or *reuse* techniques. Recycling involves the recirculation of process water to the process it was generated by. This usually requires the application of a basic treatment technique or the removal of a blowdown, to prevent the build up of suspended solids and metals in the recycling system. Where not practicable, water should be *reused*. This involves the recirculation of water for use in a process other than it was generated by. In practice several liquid effluent streams are usually fed into the same

system, pre-treated to prevent the build-up of suspended solids and metals, and then used in a variety of process applications.

Process integrated measures to limit the volume of effluent also include the use of dry gas cleaning devices instead of wet gas cleaning wherever possible and the reuse of surface runoff as process water. Good management practices during operation or maintenance should be applied to minimise the pollutant load of oils and greases. The effectiveness of the end of pipe treatment may be improved by separating cooling water from e.g. process water with a higher pollutant load. Effluents containing cadmium, mercury, or other harmful substances at higher concentration levels should be pretreated before they are discharged to the final treatment plant.

### ***End of pipe treatment***

Contaminated water generated by the non-ferrous metal industry is usually characterised by the presence of elevated metal concentrations (for example lead, copper, tin, zinc, cadmium, mercury, and chromium) as well as suspended solids. So the end of pipe treatment techniques used in the plants have been selected in order to minimise the concentration of these pollutants in final effluent discharges to the aquatic environment. The treatment of the waste water of the whole facility is usually done in a central waste water treatment plant but depending on the site specific conditions plants can be connected to an urban waste water system where the end of pipe treatment is applied. Because of different pollutant loads, the effectiveness of the end of pipe treatment may be improved by separating cooling water, surface runoff water from roofs and roadways and stockyard as well as process water or by use and reuse of water in decades depending from the demands for the water to be used.

If the treatment is carried out at the plant site, the waste water from the different production plants is usually brought together in a collecting tank. If necessary, surface water is collected in a separate tank and is then usually supplied to the collecting tank to guarantee a more constant flow. Only a few companies treat their surface water in an extra facility. The tank for the surface water has to be dimensioned to handle also storm water rainfalls. In the collecting tank, oil, grease and plastics are removed mechanically. The subsequent treatment is based on chemical precipitation and neutralisation, sedimentation and filtration or centrifugation. Devices for waste water treatment are described in Table 4-3.

**Table 4-3: Main devices for waste water treatment**

Process step	Principle	Device	Remark
Precipitation and neutralisation	<b>Chemical precipitation:</b> forming of insoluble complexes by addition of precipitants, adjustment of pH	Precipitation reactor, tanks	To remove heavy metals, hydroxides and sulphides are used as precipitants; ferric sulphate may be used to eliminate the surplus sulphide
Solids separation	<b>Sedimentation:</b> Settling due to gravity, often use of additional flocculants	Clarifier, two compartment tank, cyclators	Flocculants: polymers
Polishing step	<b>Filtration</b>	Gravity filter	
Precipitate dewatering	<b>Filtration, centrifugation</b>	Belt filter, vacuum filter (rotary drum filter), filter press, cyclone	Dewatered sludge is recycled to the metal production process or dumped

Especially where large discharges of effluent with high or low pH are possible, consideration should be given to a two or three stage pH control system. Dosing systems are unable to cope with effluent with extreme pH; therefore, an intermediate facility capable of storing acidic or alkaline effluent should be installed with an automatic control, if such effluents are likely. For highest demands, self-redundant systems should be used. Final discharges should be monitored at a minimum flow-rate, pH-value as well as temperature, and, if necessary, for other components of interest. In selecting an appropriate separation technique, consideration should be given to such factors as:

- current industry practice for the same or similar waste waters;
- ability to produce an effluent with the desired characteristics;
- characteristics of the concentrated solids that are produced;
- mechanical simplicity;
- reliability of equipment operation;
- controllability of the process;
- space requirements, and
- investments and operating costs.

#### **4.1.3 Management of by-products and waste**

As shown in Chapter 2 and 3, solid materials arise during the production of non-ferrous metals in the different process units, mainly:

- slags, mattes and drosses removed during pyrometallurgical processes,
- dust recovered from dry gas cleaning,
- solids from leaching processes,
- solids generated by the preparation of secondary feedstock and
- sludge from liquid effluent treatment.

In the following it is mainly dealt with measures and techniques for the recycling/reuse of solid materials generated and for the minimisation and handling of waste.

In lead and zinc production, only small amounts of waste material arise compared to the throughput of raw materials, because it has traditionally been the objective of the processing technology to produce as many constituents as possible in a marketable form and thereby to close the material cycle. This may be done within one company or in co-operation with other companies. The various chemical and physical properties of the substances are used to extract the individual constituents. These are, for example:

- distribution of substances between the molten and gas phase: components as tin, cadmium, arsenic, zinc, lead and their compounds, in particular, are volatilised, discharged from the production process with the off-gas and collected in gas cleaning plants in the form of flue dusts and extracted from the latter,
- different distribution coefficients of molten materials in non-miscible molten phases (for example, matte and slag),
- non-miscibility and insolubility of solid phases in liquid phases: separation of solid substances from melts (for example liquations, dross, skimmings) or from aqueous solutions (sludges, precipitates).

In this way, even traces of substances in the raw materials can be obtained in a marketable form, as shown in the following for the lead production industry: In primary lead production the concentrates contain mainly lead, iron, zinc and sulphur and in minor concentrations precious metals. Silica or lime are added as a flux. Consequently, besides lead, iron silicate slag, sulphuric acid, and Doré silver are produced. Sulphuric acid is widely used e.g. in the chemical industry. The iron silicate slag is normally granulated and can be used as a construction material (as a substitute for special sand qualities). In any case, the slag production is carried out with regard to common product standards, such as DIN EN ISO 11 126 Part 3 and VBG 48 for blasting materials as well as [109] and different technical guidelines for construction materials. The same passes for iron silica-slag from secondary production, which has a similar chemical and mineral composition and which can be used in the same fields of application.

Other by-products from primary and secondary lead production are mattes, drosses, spent battery acid, flues dusts, Calomel. Metal wastes arise only if the demand is not sufficient, which is the case for e.g. cadmium or arsenic. In this case the surplus tonnage is safely disposed in special dumps.

Other wastes which cannot be avoided are sludges from the waste water treatment plants or from the cooling water treatment, sweepings from paved areas and plants, used operation materials such as filter materials, conveyor belts, pallet wood, paper, oils, emulsions, ion exchangers from the boiler feed-water treatment, packaging materials, insulating materials,

furnace linings etc. If possible, those wastes should be used in recovery operations. Typically sludges from the waste water treatment plant, sweepings from paved areas and plants, filter materials and insulating materials are recirculated to the smelter. According to the European guideline 75/442/EEC, recovery operations are

- R 1: Use as a fuel (other than in direct incineration) or other means to generate energy
- R 2: Solvent reclamation / regeneration
- R 3: Recycling / reclamation of organic substances which are not used as solvents
- R 4: Recycling / reclamation of metals and metal compounds, etc.

This means wastes can be utilised in a material manner or can be used for the generation of energy. Priority should be given to this kind of utilisation with less environmental impact. Only if recovery is not possible according to the rules and without causing damage, should wastes be disposed of. This should be done in an approved manner in adequate facilities at the production site or at the nearest available site and it should be specified how the accumulation and storage of waste has to be controlled.

#### **4.1.4 Energy aspects**

In general, the optimal solution in terms of energy technology depends on the specific conditions existing at the site. According to the German Umweltbundesamt [87], an appropriate way of finding this solution is to draw up an energy utilisation concept which combines technical and economic objectives and eliminates information deficits. This general concept specifies economically feasible measures to be taken to optimise energy use and is structured as follows [87]:

1. An overview of the plants operated at the site and of their energy demand in terms of fuel and power demand.
2. Information on energy use inside the plants prior to site-specific optimisation, particularly
  - types and amounts of energy supplied to and removed from the plant, the most important reactions and their enthalpies including main parameters,
  - description of the plant; energy balance, flow charts.
3. Description of energy use inside the plant after its energetic optimisation (as under 2. above), including description of envisaged measures.

Certain measures are applied in the zinc and lead production industry in order to minimise energy consumption or to recover waste heat that is produced. In the processes, the fuel value of the feed material is used to decrease the amount of energy supply needed. Hot charging of intermediate products where possible or continuously working plants minimise the additional energy supply, since the material has not to be remelted in every process step. The surplus reaction heat can be used as substitute for fossil fuel or to melt additional scrap or internal reverts.



The utilisation of waste heat has a long tradition for some types of furnaces, but in some cases it is difficult, with the result that no effective solutions exist today for various sub-regions. In general the devices for using waste heat are designed in order to maintain plant availability, so they are not optimised with regard to maximising energy efficiency.

#### **4.1.5 Noise aspects/abatement techniques**

In the planning and operation of installations, all technical, structural, organisational and planning-related measures must already be taken into account during the planning phase, in a manner appropriate to the respective local operating situation and in consultation with acoustic experts. Acoustic experts should be consulted throughout construction and their advice should be taken into particular account. Use should primarily be made of technical and planning-related noise prevention measures. In general, the following have to be considered:

##### ***Technical measures***

- Obtaining information at an early stage about noise emissions of machinery, installations and parts thereof, and of work and production processes,
- use of low-noise machines and processes,
- reduction of noise generation and transmission,
- reduction of sound emission of, e.g. by the use of sound absorbers, and
- maintenance of machinery and soundproofing equipment.

##### ***Structural measures***

By means of secondary soundproofing measures such as encapsulation, absorbing walls and buildings, further noise reduction can be achieved. The absorption of air-borne sound by space-enclosing structural components primarily depends on their surface area and good sealing. Structural measures to reduce the transmission of structure-borne sound (e.g. partition joints, appropriate foundations) are necessary if a high level of structure-borne sound is expected to emanate from the building as a result of e.g. noise emission from machinery, rolling operations or vibration.

##### ***Organisational and planning-related measures***

Additional reductions in noise emissions as a function of local conditions can be achieved by organisational and planning related measures, such as accumulating high-noise sources and increasing the distance between noise sources and affected areas. In addition, operation restrictions may have to be imposed in special cases to reduce noise emissions. The exploration of suitable sites under consideration of the existing noise sources is of particular importance. Noise emissions from traffic to and from installations, which arise in connection with their operation must likewise be taken into account.

#### **4.1.6 Plant safety aspects**

According to the German Umweltbundesamt [87], the general policy for the prevention of, preparedness for and response to industrial accidents is based on the following principles:

##### ***Prevention principle***

- The plant should be constructed and operated in such a way as to prevent the uncontrolled development of normal operation,
- the plant should be constructed and operated in such a way that consequences of accidents are reduced,
- the plant should be constructed and operated according to the best available safety techniques (state of the art safety technology).

##### ***Consideration of complex systems in process industries***

Complex systems can only be sufficiently examined by means of systematic, logical methods. This is taken into account by applying system-analytical investigation methods and detailed safety analysis considering the conditions of the individual case.

##### ***Appropriateness of means***

Safety requirements are graded according to "type and scope of hazards to be expected". To this end, rules are set up for substances relevant to accidents (substance criteria, list of substances) and industrial activities relevant to accidents (list of plants). The objective dependence of the disaster potential upon the quantity of hazardous substances is considered by a quantity threshold concept that defines staged safety requirements as a function of quantity [87].

#### **4.1.7 Plant operation and decommissioning**

Operational control plays an important role in the reduction of emissions. Special attention should be paid to the maintenance of equipment, malfunctions and breakdowns as well as supervision and training [114]. With regard to the cessation of activities, and in order to avoid any pollution risk and to return the site of operation to a satisfactory state, soil protection is of major importance.

According to German Umweltbundesamt [87], an integrated approach requires that at least the following precautions have to be taken:

- 1) to minimise the amount of soil that needs to be excavated or replaced due to construction measures and to make sure that excavated soil material is treated carefully (in order to avoid harmful changes of soil properties),
- 2) to minimise the additional input of substances into the soil during the operation phase of a facility (e.g. additional input due to deposition of airborne substances should not lead to precautionary soil levels being exceeded and spillages should be avoided),
- 3) to ensure a clean closure when a facility is shut down, e.g. cleaning up and rehabilitation of contaminated soil, cleanup or securing of environmental hazards of hazardous landfills, with regard to the future use of the area. Natural soil functions should be safeguarded, if feasible.

#### **4.1.8 Measurement of emission values**

The following section is intended to ensure that the emissions specified in the whole report and in Chapters 4.2 and 4.3, in particular, are measured in such a way that the results are representative, mutually comparable and clearly describe the relevant operating state of the plant.

##### ***Measurement Planning***

The objective and scope of measurements are governed by the requirements in the approval decision or by particular events. In principle, the measurements serve to determine substances in the clean gas. Measurement planning should take account of the mode of operation and the operating state of off-gas purification plants, operating conditions in the plant (continuous, discontinuous, start-up and shut-down operations, load change) and the effect of thermodynamic interference factors. These data form the basis for determining the selection of operating conditions at which the highest emissions will presumably be recorded, the number and duration of the measurements, the method of measurement to be chosen, and the position of the measurement locations and points.

In the case of continuous and batch-wise operation, a sample collection time or measurement time of half an hour (half-hour mean value) is, as a rule, necessary. If dust contents are low or if PCDD/PCDF are to be determined, other measurement times and, consequently, other reference times may be necessary because of the limitation of detection. In particular cases, for example batch operation, the measurement time and, consequently, the averaging time should be appropriately modified. For continuous operation and only slight fluctuations in the emission characteristics, at least 3 individual measurements should be performed at the highest emission level. If it is anticipated that the emission level will be very variable during continuous operation, at least 6 measurements should be carried out, the sampling and averaging time being limited to the emission phase.

### ***Sampling Locations***

The sampling points should meet the requirements of Guidelines VDI 2066 Part 1 [93] and VDI 2448 Part 1 [98]. According to the latter, the sampling points

- should be clearly marked,
- should, if possible, have a disturbance-free flow in the measurement section,
- should have measurement openings that can be closed,
- should have the required energy supplies,
- should have sufficiently large working platforms, and
- should ensure that the requirements for safety at work are met.

### ***Measured Variables, Methods of Measurement and Instruments***

Measurements of the components specified in Table 4-4, where the VDI guideline is quoted in which the methods of measuring the components are described, should be carried out to characterise the emission behaviour of a plant, where the off-gas is removed via a known outlet:

**Table 4-4: VDI guidelines on emission measurements**

<b>Component</b>	<b>VDI Guideline or DIN Standard</b>
Total dust	VDI 2066 [93]
Dust constituents Cd, Cr, Cu, Pb, Zn	VDI 2066 [93] VDI 2268 [95]
As	VDI 2066 [93] VDI 2268 [95]
Total organic carbon	VDI 3481 [100]
Sulphur dioxide	VDI 2462 [99]
PCDD/PCDF	DIN EN 1948 [22], VDI 3499 [102]

The parameters sulphur oxides (mass flow > 50 kg/h) and total dust (mass flow > 2 kg/h) should be continuously observed using an approved measurement apparatus, the suitability of which has been tested and, as a rule, evaluated using an emission evaluation computer.

The reference quantities necessary for evaluating and assessing the continuous measurement should also be continuously observed. The continuous measurement of these parameters may be dispensed with, if experience shows they are subject to only small fluctuations. The instruments should be calibrated after installation of a measurement location and then every 5 years, and should be checked once a year for serviceability.

### ***Reference Quantities***

To convert the emission concentrations obtained to standard conditions ( $p_o = 1,013 \text{ hPa}$ ,  $T_o = 273 \text{ K}$ ,  $p(\text{H}_2\text{O}) = 0 \text{ hPa}$ ), the volumetric off-gas flow (in order to calculate the emission mass flow), the off-gas temperature, the water vapour content of the off-gas, the static pressure in the off-gas duct and the atmospheric pressure shall be determined as off-gas parameters.

***Measurement Result Evaluation and Measurement Report***

All the emission measurement results shall be reported as masses, in  $\text{mg}/\text{m}^3$  or, for PCDD/PCDF, in  $\text{ng-TE}/\text{m}^3$ , of the emitted components, relative to the volume of the off-gas in the standard state after subtracting the water vapour content. From the measured values of instantaneous samples for gaseous components, the measurement result should be determined as a half-hour mean value or as a computed half-hour mean value. From the measured values of individual measurements of particulate emissions, the measurement result should be reported as a half-hour mean value or, if the sampling time is longer, as a mean value for the sampling time.

***Continuously determined measurement should be evaluated as follows:***

From the measured values, the half-hourly mean value should always be determined for each consecutive half hour. The half-hourly mean values should, if necessary, be converted to the respective reference quantities, assigned to at least 20 class intervals and stored as a frequency distribution. A daily mean value for the daily operating time should be calculated from the half-hourly mean values for each day of the year. The emission limits are deemed to be met if non of the daily mean values exceed the specified concentration by mass, 97 % of all the half-hourly mean values do not exceed 6/5 of the specified concentration by mass and non of the half-hourly mean values exceed twice the specified concentration by mass.

Any measurement report and measurement protocol drawn up should conform to Guideline VDI 2066 Part 1 [93] and should in particular contain:

- the objective,
- general information on the measurements,
- a description of the plant, its state and operating data,
- operating conditions during the measurement,
- information on the measurement planning,
- sampling locations,
- methods of measurement,
- tabular presentation of the individual measurements,
- evaluation of the results,
- consideration of errors,
- presentation of the quality assurance measures, and
- an abstract.



## 4.2 German Candidate BAT for zinc production

Within the framework of integrated pollution prevention and control, first of all the above-mentioned *general techniques and rules* as described in Chapter 4.1 should be considered for each plant operation. Additionally, for zinc production plants several *process* as well as *plant specific* abatement techniques have proven their suitability for integrated pollution prevention and control. Techniques showing this potential have been considered as candidate BAT, too.

In the following sections, the techniques applied in the German zinc industry are reviewed and a list of these candidates BAT (CBAT) is presented for each of the main production processes. The achieved emission levels and emission load levels are based on the following definitions:

### ***Achieved emission level (air):***

This level gives the range of daily average emission values, determined on the basis of half-hour mean values<sup>21</sup>, of a contaminant in an off-gas flow [mg/Nm<sup>3</sup>]. Guidelines for the measurement of emission values are described in Section 4.1.8 and [4]. The given emission levels have been achieved in plants using the candidate best available techniques (described in this report in Chapter 3 and 4) over a long period of normal operation. It has to be mentioned, that the range of achieved emission levels based on daily average emission values is well below the emission limit values set in permits i.e. as half-hour mean values. Depending from process and abatement technologies the ratio between the given achieved emission levels and the set emission limit values in permits is up to 0.1.

### ***Achieved emission load level (air):***

This value gives the product-specific *emission load* [g/t], calculated as a product of the *average annual emission value* of a contaminant [mg/Nm<sup>3</sup>], the average off-gas volume [Nm<sup>3</sup>/h] and the annual operation time [h/a], related to production capacity [t/a].

### ***Achieved emission level (waste water):***

This level gives the range of average concentration values of a contaminant [mg/l] determined as 2 hours composite samples or as qualified random sample. Guidelines for the measurement of concentration values are described in Section 7.1.2.2 and [1]. The given emission levels have been achieved in plants using the candidate best available techniques (described in this report in Chapter 3 and 4) over a long period of normal operation. It has to be mentioned, that the range of achieved emission levels based on daily average emission values is well below the emission limit values set in permits i.e. as two hours composite samples or qualified random samples. Depending from process and abatement technologies the ratio between the given achieved emission levels and the set emission limit values in permits is up to 0.1.

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<sup>21</sup> If the dust contents are low, other measurement times and, consequently, other reference times may be necessary because of the limitation of detection (c.f. Section 4.1.8).

***Achieved emission load level (waste water):***

This value gives the product-specific *emission load* [g/t], calculated as a product of the *average emission value* of a contaminant [mg/l], the average discharge volume [m<sup>3</sup>/h] and the annual operation time [h/a], related to production capacity [t/a].

An overview of the structure of Chapter 4.2 is given in Table 4-5.

**Table 4-5: Structure of Chapter 4.2 (overview)**

Main plants	Section	Characterisation	CBAT	Achieved emission level
Zinc electrolysis	4.2.1	4.2.1.1	Air (4.2.1.2) Water (4.2.1.3) Recycling/waste (4.2.1.4) Energy (4.2.1.5)	Air/water (4.2.1.6)
Imperial Smelting furnace	4.2.2	4.2.2.1	Air (4.2.2.2) Water (4.2.2.3) Recycling/waste (4.2.2.4) Energy (4.2.2.5)	Air/water (4.2.2.6)
New Jersey zinc refining	4.2.3	4.2.3.1	Air - water - recycling/ waste - energy (4.2.3.2)	Air/water (4.2.3.3)
Waelz kiln	4.2.4	4.2.4.1	Air (4.2.4.2) Water (4.2.4.3) Recycling/waste (4.2.4.4) Energy (4.2.4.5)	Air/water (4.2.4.6)
Fuming reactor	4.2.5	4.2.5.1	Air - water - recycling/ waste - energy (4.2.5.2)	Air (4.2.5.3)
Remelting	4.2.6	4.2.6.1	Air - water - recycling/ waste - energy (4.2.6.2)	Air (4.2.6.3)
<b>Further plants</b>				
New Jersey retort	4.2.7	4.2.7.1	Air - water - recycling/ waste - energy (4.2.7.2)	Air/water (4.2.7.3)



### 4.2.1 Zinc electrolysis plants

In the following, first a general characterisation of the zinc electrolysis process is given. Then, the *specific* abatement techniques applied in German zinc electrolysis plants are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

#### 4.2.1.1 Characterisation

A general characterisation of zinc electrolysis process is given in Table 4-6.

**Table 4-6: Characterisation of the zinc electrolysis process**

Criteria	Assessment
<b>Relevance</b>	The zinc electrolysis is the pre-dominate process for zinc production in the EU. A total share of 80% and above is produced in 12 electrolysis plants [49].
<b>Flexibility concerning raw material use</b>	The main input materials are sulphidic zinc concentrates. Only small amounts of secondary raw materials can be processed.
<b>Products</b>	Besides high purity zinc (SHG) as main product, sulphuric acid and cadmium are produced.
<b>By-products</b>	Lead-silver concentrate is used for recovery of silver and zinc Zinc-iron intermediate used for zinc/lead production with subsequent silver recovery
<b>Environmental concerns:</b> Waste generation	Dumping of Jarosite Mercury containing residue from sulphuric acid plant

#### 4.2.1.2 CBAT for the abatement of air pollution

The main emissions into the atmosphere from zinc electrolysis plants are gaseous substances, particulate matter, fumes and volatiles as shown above. These emissions consist of sulphur dioxide and other sulphur compounds, as well as metals and metal compounds. In Table 4-7, CBAT for the abatement of air pollution from zinc electrolysis plants are summarised.

**Table 4-7: CBAT for abatement of air pollution in zinc electrolysis plants**

No.	Abatement techniques	Assessment (Effects, applicability, ...)
<b>Process unit(s): Raw materials handling/roasting/roast gas cleaning</b>		
<b>a1</b>	Enclosurement of the roaster shop and the calcine classification mill	Reduction of fugitive emissions
<b>a2</b>	Suction ventilation system for collecting emissions from calcine coolers, ballmill, start-up phase roaster, ambient air roaster shop	Reduction of fugitive emissions
<b>a3</b>	Exhaust gases are cleaned in a bag filter	Removal of dust for recycling
<b>a4</b>	Roast gas cleaning with cooling, dedusting (cyclones, hot ESP), scrubbing, wet ESP	Removal of dust
<b>a4</b>	Further treatment of roast gas (e.g. Boliden/Norzink process)	Precipitation of mercury vapour
<b>a5</b>	Further roast gas processing in a sulphuric acid plant	Sulphur recovery
<b>Process unit(s): Sulphuric acid plant</b>		
<b>b1</b>	Double catalysts acid plant (e.g. four-layer vanadium oxide SO <sub>2</sub> -converter / double contact SO <sub>3</sub> absorber)	Conversion of SO <sub>2</sub> with an efficiency of more than 99.6%
<b>b2</b>	Multiple tube filters	Removal of acid mists
<b>Process unit(s): Leaching plant/purification/hydrometallurgical cadmium plant</b>		
<b>c1</b>	Central gas scrubbing system for exhaust gases from all reactors	Prevention of aerosol emissions, metals
<b>c2</b>	Scrubbing of exhaust gas with strong oxidative medium if the risk of arsine emissions occurs	Removal of arsine and other metal compounds
<b>Process unit(s): Electrolysis</b>		
<b>d1</b>	Ventilation of cooling towers	Prevention of fugitive mist emissions
<b>d2</b>	Ventilation of the whole cellhouse	Prevention of fugitive mist emissions
<b>d3</b>	Mist collectors for the treatment of exhaust air	Prevention of mist emissions
<b>Process unit(s): Cadmium plant/cadmium refinery</b>		
<b>e1</b>	Permanent air exhaustion for cadmium furnace, smelter, caster, ...	Prevention of fugitive emissions
<b>e2</b>	Exhaust gas scrubbing	Removal of metal compounds
<b>e3</b>	Dry gas cleaning using ESP for exhaust gases from the furnaces, distillation column, casting section	Removal of dust for recycling
<b>Process unit(s): Melting/(alloying)/casting</b>		
<b>f1</b>	Central bag filter for off-gas cleaning from electric induction furnaces	Removal of dust for recycling

#### 4.2.1.3 CBAT for the reduction of water consumption and the control and treatment of waste water

In Table 4-8 CBAT for the reduction of water consumption and the control and treatment of waste water are summarised.

**Table 4-8: CBAT for the reduction of water consumption and treatment of waste water**

No.	Techniques	Assessment (Effects, applicability,...)
w1	Adequate waste water treatment	The water treatment scheme is described in 4.1.
w2	Collection of rain water and internal use	Reduction of fresh water consumption
w3	Effluents from roast gas cleaning are treated in the central waste water treatment plant	-

#### 4.2.1.4 CBAT for the recycling of solid materials, waste prevention and the handling of waste

In Table 4-9 main techniques for the recycling of solid materials, waste prevention and the handling of waste are summarised.

**Table 4-9: CBAT for the recycling of solid materials, waste prevention and handling of waste**

No.	Techniques	Assessment (Effects, applicability,...)
s1	Change/choice of input materials	Change of feedstock composition, but this measure is limited due to the availability of raw materials
s2	Recovery of mercury from roast gas	Production of Calomel
s3	Precipitation of copper, cadmium, cobalt by addition of zinc dust	Recovery of copper, cadmium, cobalt
s4	Processing of cadmium briquettes by distillation	Production of high grade cadmium
s5	External treatment of lead-silver concentrate in pyrometallurgical lead production plants	Recovery of lead and silver
s6	Recycling of sludges (from waste water treatment) to a lead production plant	Minimisation of waste, but the applicability is limited so that the remaining part has to be dumped
s7	Basic principles in the field of waste management (safe disposal of Jarosite in specialised ponds)	-
s8	Omission of hot leach and recycling of zinc-iron intermediate from leaching	Zinc-iron intermediate can be processed external (IS furnace, waelz process) for zinc recovery, but the applicability is limited due to the IS furnace capacity
s9	Internal recycling of dross from casting	Reuse

#### 4.2.1.5 CBAT for the reduction of energy consumption

In Table 4-10 the main techniques for the reduction of energy consumption are summarised.

**Table 4-10: CBAT for the reduction of energy consumption and heat recovery**

No.	Techniques	Assessment (Effects, applicability, ...)
<b>h1</b>	Waste heat boiler for heat recovery from roast gas	Production of high pressure steam

#### 4.2.1.6 Achieved emissions levels in zinc electrolysis plants

In Table 4-11, achieved emission levels and emissions load levels for German zinc electrolysis plants are listed.

**Table 4-11: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h]/[Nm <sup>3</sup> /t zinc]	Emission load level [g/t zinc]
Transport and grinding of calcine	Dust: 0.6 - 10 Zn: 0.3 - 5 Cd: 0.002 - 0.015	12,000 - 22,000 / < 1,600	Dust: 0.7 - 1.0 Zn: 0.4 - 0.6 Cd: < 0.002
Sulphuric acid plant	SO <sub>2</sub> : 900 - 1,600	35,000 - 60,000 / 3,000 - 4,000	SO <sub>2</sub> : 2,600 - 4,200 SO <sub>3</sub> : 500
Leaching and purification	Zn: 0.1 - 0.5 Cd: 0.01 - 0.2	65,000 - 80,000 / 4,000 - 7,000	Zn: 0.5 - 1.4 Cd: < 0.02 - 0.05
Electrolysis plant (cooling towers )	Zn: 0.1 - 1.0	800,000 - 1,650,000 / 85,000 - 115,000	Zn: 4.1 - 8.6
Melting, alloying, casting	Zn: 0.5 - 5.0	38,000 - 70,000 / 2,500 - 4,000	Zn: 2.0 - 5.0

In Table 4-12, achieved emissions levels for waste water discharges are summarised. A typical waster water flow is about 25 - 40 m<sup>3</sup>/h.

**Table 4-12: Achieved emission levels for waste water discharges**

Element	Emission level <sup>*)</sup> [mg/l]	Load level <sup>*)</sup> [g/t zinc]	Element	Emission level <sup>*)</sup> [mg/l]	Load level <sup>*)</sup> [g/t zinc]
Cu	< 0.5	< 10	As	< 0.1	< 2
Pb	< 0.5	< 15	Ni	< 0.5	< 15
Zn	< 1	< 30	Cr	< 0.5	< 10
Cd	< 0.2	< 3	Sulphide	< 1	n. a.
Hg	< 0.05	< 1	AOX	< 1	n. a.

<sup>\*) Remark:</sup> The emission levels and the emissions load levels given in Table 4-12 are minimum requirements of the German *Abwasserordnung*, Annex 39 ([13] and [110]). Actual figures of the two German zinc electrolysis can be found in Chapter 3.1.1.

## 4.2.2 Imperial Smelting furnace plant

In the following, first a general characterisation of the Imperial Smelting furnace plant is given. Then, the *specific* abatement techniques applied in the German IS furnace plant are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

### 4.2.2.1 Characterisation

A characterisation of Imperial smelting process is given in Table 4-13.

**Table 4-13: Characterisation of the Imperial smelting process**

Criteria	Assessment
<b>Relevance</b>	The IS furnace is the main pyrometallurgical zinc production process with four plants operated in the EU [49].
<b>Flexibility concerning raw material use</b>	Besides zinc/lead concentrates, a wide range of different secondary raw materials can be processed with the sinter plant, the hot briquetting plant and by direct injection.
<b>Products</b>	Raw zinc for further refining Lead bullion for further refining Sulphuric acid
<b>By-products</b>	Iron silicate slag with low leachability Cadmium fraction
<b>Environmental concerns:</b> Utilisation of by-products Waste generation Energy	Slag reduction Mercury containing residue Total use of LCV gas

### 4.2.2.2 CBAT for the abatement of air pollution

In Table 4-14 CBAT for the abatement of air pollution from IS furnace plants are summarised.

**Table 4-14: CBAT for the abatement of air pollution**

No.	Abatement techniques	Assessment (Effects, applicability, ...)
<b>Process unit(s): Sinter plant/roast gas cleaning</b>		
<b>a1</b>	Roast gas cleaning with Hot ESP, wet scrubber, and wet ESP	Precipitation of dust and metals
<b>a2</b>	Further treatment of roast gas (Boliden/Norzink process)	Precipitation of mercury vapour
<b>a3</b>	Wet ESP for final dedusting	Final purification
<b>a4</b>	Further roast gas processing in a sulphuric acid plant	Recovery of sulphur
<b>a5</b>	Exhaust gas cleaning with bag filters	Precipitation of dust
<b>a6</b>	Collection of exhaust gases from sinter cooling/breaking	Reduction of fugitive emissions
<b>Process unit(s): Sulphuric acid plant</b>		
<b>b1</b>	Double catalysts acid plant (e.g. four-layer vanadium oxide SO <sub>2</sub> -converter / double contact SO <sub>3</sub> absorber)	Conversion of SO <sub>2</sub> with an efficiency of more than 99.6%
<b>b2</b>	Filters	Removal of acid mists
<b>Process unit(s): Cadmium plant</b>		
<b>c1</b>	Transport of wet cadmium containing dust	Prevention of fugitive emissions
<b>Process unit(s): Hot briquetting plant</b>		
<b>d1</b>	Fabric filter for off-gas cleaning	Dust removal
<b>d2</b>	Subsequent activated coke filter	Minimisation of PCDD/PCDF emissions
<b>Process unit(s): IS furnace/spray condenser/zinc-lead separator/gas cleaning/slag treatment</b>		
<b>e1</b>	Double bell	Reduction of fugitive emissions
<b>e2</b>	Wet ESP for cleaning of collected fugitive emissions from top furnace area and slag granulation	Precipitation of dust
<b>e3</b>	Desintegrator for IS process gas cleaning	-
<b>e4</b>	Fabric filter for exhaust gas cleaning (secondary dedusting furnace area)	Reduction of fugitive emissions
<b>Process unit(s): Refinery</b>		
see New-Jersey refining plants (c.f. 4.2.3)		

#### 4.2.2.3 CBAT for the reduction of water consumption and the control and treatment of waste water

In Table 4-15 CBAT for the reduction of water consumption and the control and treatment of waste water are summarised.

**Table 4-15: CBAT for reduction of water consumption and treatment of waste water**

No.	Techniques	Assessment (Effects, applicability,...)
<b>w1</b>	Use of a central waste water treatment plant	The water treatment scheme is described in 4.1.
<b>w2</b>	Pre-treatment of effluent from roast gas cleaning (final treatment in the central waste water plant)	Reduction of emission load for central treatment plant.
<b>w3</b>	Precipitation of thallium as pre-treatment step for waste water from the cadmium plant	Reduction of emission load for central treatment plant.

#### 4.2.2.4 CBAT for the recycling of solid materials, waste prevention and the handling of waste

In Table 4-16 main techniques for the recycling of solid materials and the prevention of waste are summarised.

**Table 4-16: CBAT for the recycling of solid materials and prevention of waste**

No.	Techniques	Assessment (Effects, applicability,...)
s1	Recovery of cadmium from roast gas cleaning	Upgrading of the cadmium fraction, but the market for cadmium/cadmium compounds is limited.
s2	Recovery of mercury from roast gas	Production of Calomel, but the market for Calomel is limited.
s3	Internal recycling of lead containing residue from the cadmium plant	Recovery of lead and zinc
s4	Use of loaded coke from gas cleaning as fuel in the IS furnace	Reduction of fuel consumption
s5	Granulation of IS furnace slag	Production of a marketable by-product (road construction)
s6	Internal recycling of sludge from the waste water plant	Recovery of zinc and lead

#### 4.2.2.5 CBAT for the reduction of energy consumption

In Table 4-17 the main techniques for the reduction of energy consumption are summarised.

**Table 4-17: CBAT for the reduction of energy consumption and heat recovery**

No.	Techniques	Assessment (Effects, applicability,...)
h1	Waste heat boiler for heat recovery from off-gases from the refinery	Steam production
h2	Internal use of IS furnace off-gas (coke preheating, cowper operation)	Reduction of energy consumption

#### 4.2.2.6 Achieved emissions levels in Imperial Smelting furnace plants

In Table 4-18, achieved emission levels and emissions load levels for the German IS furnace plant are listed.

**Table 4-18: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level <sup>*)</sup> [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t zinc]	Emission load level [g/t zinc]
Charging	Dust: 1 - 6 Zn: 0.3 - 1.8 Cd: 0.003 - 0.018 Pb: 0.18 - 1.1	90,000 / 7,500	Dust: 25 Zn: 8 Cd: < 0.1 Pb: 5
Sinter plant	Dust: 2 - 10 Zn: 0.6 - 3 Cd: 0.006 - 0.03 Pb: 0.3 - 1.8 SO <sub>2</sub> : < 800	120,000 / 10,000	Dust: 58 Zn: 17 Cd: 0.2 Pb: 10 SO <sub>2</sub> : < 7,500
Sulphuric acid plant	SO <sub>2</sub> : < 730	66,000 / 4,000 - 5,000	SO <sub>2</sub> : < 4,000 SO <sub>3</sub> : 500
Slag treatment	Dust: 3 - 9 Zn: 1.6 - 5 Cd: 0.003 - 0.009 Pb: 0.45 - 4 SO <sub>2</sub> traces	70,000 / 4,000	Dust: 33 Zn: 18 Cd: < 0.05 Pb: 10 SO <sub>2</sub> : < 0.01
Hot Briquetting	Dust: < 1.0 Zn: < 1.0 Cd: < 0.001 Pb: < 1.0	45,000 / 3,500	Dust: < 3.5 Zn: < 3.5 Cd: < 0.01 Pb: < 3.5
IS furnace	Dust: 1 - 5 Zn: 0.55 - 2.7 Cd: 0.001 - 0.005 Pb: 0.1 - 0.5	100,000 / 8,000	Dust: 24 Zn: 13 Cd: < 0.05 Pb: 2.4

<sup>\*)</sup> To guarantee, that the *emission limit values* can be kept, the mentioned *emission level* has to be about 3 - 10 times lower than the *emission limit value* (c.f. Chapter 4.2).

In Table 4-19, achieved emissions levels for waste water discharges are summarised. A typical waste water flow is about 380 - 420 m<sup>3</sup>/h.

**Table 4-19: Achieved emission levels for waste water discharges**

Element	Emission level [mg/l]	Load level [g/t zinc]	Element	Emission level [mg/l]	Load level [g/t zinc]
Cu	0.006	< 0.2	As	0.02	< 0.7
Pb	0.1	< 3.5	Ni	0.003	< 0.1
Zn	0.2	< 7	Cr	0.001	< 0.05
Cd	0.008	< 3	Cyanide	< 0.1	< 3.5
Hg	0.006	< 0.2	Sulphide	< 0.1	< 3.5

<sup>\*)</sup> To guarantee, that the *emission limit values* can be kept, the mentioned *emission level* has to be about 10 times lower than the *emission limit value* (c.f. Chapter 4.2).



### 4.2.3 New-Jersey zinc refining plants

In the following, first a general characterisation of the New-Jersey zinc refining process plants is given. Then, the *specific* abatement techniques applied in the German New-Jersey zinc refining plants are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

#### 4.2.3.1 Characterisation

A general characterisation of the New-Jersey zinc refining process plants is given in Table 4-20.

**Table 4-20: Characterisation of the New-Jersey zinc refining process plants**

Criteria	Assessment
<b>Relevance</b>	The New-Jersey rectification process is the main zinc refining process in the EU, operated in six plants [49].
<b>Flexibility concerning raw material use</b>	Raw zinc and all kinds of metallic zinc scraps can be processed after liquation.
<b>Products</b>	SHG zinc GOB zinc Crude lead
<b>By-products</b>	Zinc-cadmium alloy
<b>Environmental concerns:</b>	-

#### 4.2.3.2 CBAT for New Jersey refining plants

In Table 4-21 CBAT for New Jersey refining plants are summarised.

**Table 4-21: CBAT for New Jersey refining plants**

No.	Abatement techniques	Assessment (Effects, applicability,...)
	<b>CBAT for the abatement of air pollution</b>	
<b>a1</b>	Bag filter for treatment of off-gases from heating chambers, refining furnaces	Off-gas dedusting
	<b>CBAT for the recycling of solid materials, waste prevention and the handling of waste</b>	
<b>s1</b>	External recycling of zinc-cadmium alloy	Recovery of zinc and cadmium
<b>s2</b>	Recycling of zinc containing filter dust	Recovery of zinc
	<b>CBAT for the reduction of energy consumption</b>	
<b>h1</b>	Recuperators for waste gas cooling	Process air preheating

### 4.2.3.3 Achieved emissions levels in New-Jersey zinc refining plants

In Table 4-22 achieved emission levels and emissions load levels for New-Jersey zinc refining plants are listed.

**Table 4-22: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level <sup>*)</sup> [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t SHG zinc]	Emission load level [g/t SHG zinc]
Refining plant	Dust: 2 - 3 Zn: 1.1 - 1.6 Cd: 0.006 - 0.009 Pb: 0.04 - 0.06	40,000 / 3,300	Dust: 6.5 - 10 Zn: 3.5 - 5.5 Cd: 0.02 - 0.03 Pb: 0.1 - 0.2

<sup>\*)</sup> To guarantee, that the *emission limit values* can be kept, the mentioned *emission level* has to be about 3 - 10 times lower than the *emission limit value*.

New-Jersey zinc refining plants can be operated effluent free.

### 4.2.4 Waelz kiln plants

In the following, first a general characterisation of the waelz kiln plants is given. Then, the *specific* abatement techniques applied in German waelz kiln plants are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

#### 4.2.4.1 Characterisation

A general characterisation of the waelz process plants is given in Table 4-23.

**Table 4-23: Characterisation of the waelz process plants**

Criteria	Assessment
<b>Relevance</b>	The waelz process is the main process for the recycling of zinc-containing dusts in the EU, operated in seven plants [49].
<b>Flexibility concerning raw material use</b>	A wide range of zinc (and lead) containing secondary raw materials can be processed and two different operation modes (acidic/basic) can be chosen. The needed physical properties (agglomeration, moisture, ...) are not very strict. The content of chlorides, alkalies and sulphides has to be controlled.
<b>Products</b>	Waelz oxide/leached waelz oxide
<b>By-products</b>	Waelz slag
<b>Environmental concerns:</b> Emissions into the atmosphere Utilisation of by-products	Advanced gas cleaning may become necessary Optimisation of waelz slag quality

#### 4.2.4.2 CBAT for the abatement of air pollution

In Table 4-24 CBAT for the abatement of air pollution from waelz kiln plants are summarised.

**Table 4-24: CBAT for the abatement of air pollution**

No.	Abatement techniques	Assessment (Effects, applicability, ...)
<b>Process unit(s): Raw materials/handling/charging</b>		
<b>a1</b>	In-house pelletising and direct feeding of fresh pellets	During a normal operation the direct feeding of fresh pellets is possible, but during a still-stand of the furnace the produced pellets of the pelletising-plant has to exposure outdoor.
<b>a2</b>	Bag filter for the transferring points of the pelletising plant, including the dust hoppers and the dosing belt conveyor	Reduction of fugitive emissions from charging
<b>a3</b>	Covered belt conveyors for dust and pellets handling	Reduction of fugitive emissions from material transport
<b>Process unit(s): Rotary kiln/gas cleaning system</b>		
<b>b1</b>	Primary hood at the furnace mouth	Reduction of fugitive emissions
<b>b2</b>	Conventional gas cleaning with dust settler, cooling, bag filter or ESP or wet gas cleaning	Precipitation of waelz oxide, removal of dust
<b>b3</b>	Venturi scrubber unit (for the preheating of water used for the waelz oxide leaching plant)	for the normal operation: de-dusting of one third of the kiln gases for fixing operations of ESP/bag filter/wet gas cleaning: dedusting of the remaining gases from the waelz kiln
<b>b4</b>	Supplement gas cleaning for the removal of mercury and PCDD/PCDF emissions, if necessary (e.g. injection of adsorbent or installation of a coke bed filter)	Reduction of mercury and PCDD/PCDF emissions
<b>Process unit(s): Slag treatment</b>		
<b>c1</b>	Hood, ventilation system	Reduction of fugitive emissions
<b>c2</b>	Injection of exhaust gases: - into the furnace - into the main off-gas stream	Reduction of dust and mist emissions
<b>Process unit(s): Waelz oxide leaching (if applied)</b>		
<b>d1</b>	Dedusting system for the soda silo	Reduction of fugitive emissions
<b>d2</b>	Exhaust filter at dry dust handling stations	Reduction of fugitive emissions
<b>d2</b>	Bag filter for the drying area	Reduction of fugitive emissions

#### 4.2.4.3 CBAT for the reduction of water consumption and the control and treatment of waste water

In Table 4-25 CBAT for the reduction of water consumption and the control and treatment of waste water are summarised.

**Table 4-25: CBAT for the reduction of water consumption and treatment of waste water**

No.	Techniques	Assessment (Effects, applicability, ...)
w1	Adequate treatment of waste water from the waelz oxide leaching plant	Purification of waste water from the waelz oxide leaching
w2	Use of settling tanks for rain water	Reduction of content of solids in the rain water
w3	Recirculation of cooling water from slag cooling (closed loop)	Reduction of water consumption

#### 4.2.4.4 CBAT for the recycling of solid materials, waste prevention and the handling of waste

In Table 4-26 main techniques for the recycling of solid materials, waste prevention and the handling of waste are summarised.

**Table 4-26: CBAT for the recycling of solid materials, waste prevention and the handling of waste**

No.	Techniques	Assessment (Effects, applicability, ...)
s1	Treatment of waelz slag	Production of granulated slag for different use options
s2	Internal recycling of solids from the waste water treatment plant and the rain water settling tanks	Elimination of waste
s3	Internal recycling of solids from sweeping and vacuum cleaning machine	Elimination of waste, clean-up of the plant soil
s4	Waelz oxide leaching	Obtained double leached waelz oxide can be sold to zinc electrolysis plants for zinc production.
s5	Recycling of used refractory material	Used refractory material can be sold back to refractory producers or crushed and recycled internally.

#### 4.2.4.5 CBAT for the reduction of energy consumption

In Table 4-27 main techniques for the reduction of energy consumption are summarised.

**Table 4-27: CBAT for the reduction of energy consumption and heat recovery**

No.	Techniques	Assessment (Effects, applicability, ...)
h1	Venturi scrubber for cooling the waelz kiln gas and heating the water for the leaching plant	Saving up to 1,200,000 kcal/h
h2	Heat exchanger for the second leaching step	Recovering of about 900,000 kcal/h. Used for the conditioning of the temperature for the waste water
h3	Primary hood at the furnace mouth	Injection of preheated air into the kiln

#### 4.2.4.6 Achieved emissions levels in waelz kiln plants

In Table 4-28, achieved emission levels and emissions load levels for waelz kiln plants are listed. As the composition of the feed materials shows strong variations, the achieved emissions load levels are given per tonne feed material.

**Table 4-28: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level <sup>*)</sup> [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t feed]	Emission load level [g/t feed]
Waelz kiln incl. slag cooling (off-gas)	Dust: 1 - 5 Zn: 0.1 - 2 Pb: 0.1 - 1 Cd: < 0.01	50,000 - 75,000 / 4,000 - 6,000	Dust: 20 - 60 Zn: 10 - 30 Pb: 2 - 6 Cd: 0.01 - 0.1

<sup>\*)</sup> To guarantee, that the emission limit values can be kept, the mentioned emission level has to be about 3 - 10 times lower than the emission limit value.

In Table 4-29, achieved emissions levels for waste water discharges from waelz kiln plants are summarised. For a feed of 6 t/h, a flow rate of 9 - 10 m<sup>3</sup>/h is obtained.

**Table 4-29: Achieved emission levels for waste water discharges**

Element	Emission level [mg/l]	Load level [g/t]	Element	Emission level [mg/l]	Load level [g/t]
Cu	< 0.5	< 2	As	< 0.1	< 0.4
Pb	0.3 - 0.5	< 2	Ni	< 0.5 - 1	< 2
Zn	0.8 - 1	< 2	Cr	< 0.5	< 2
Cd	0.05 - 0.2	< 1	Sulphide	< 1	n. a.
Hg	< 0.05	< 0.2	AOX	< 1	n. a.

#### 4.2.5 Fuming reactor plant

In the following, first a general characterisation of the fuming reactor plant is given. Then, the specific abatement techniques applied in German fuming reactor plant are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

##### 4.2.5.1 Characterisation

A general characterisation of the fuming reactor plant is given in Table 4-30.

**Table 4-30: Characterisation of the fuming reactor plant**

Criteria	Assessment
<b>Relevance</b>	One of the two fuming plants in operation in the EU is of the cyclone type.
<b>Flexibility concerning raw material use</b>	A wide range of zinc bearing raw materials (slags, residues, ...) can be processed.
<b>Products</b>	Mixed oxide Slag (inert)
<b>By-products</b>	Steam for electricity production Matte for copper production
<b>Environmental concerns:</b> Emissions into the atmosphere	SO <sub>2</sub> limit in purified gas

#### 4.2.5.2 CBAT for fuming reactor plants

In Table 4-31 CBAT for fuming reactor plants are summarised.

**Table 4-31: CBAT for fuming reactor plants**

No.	Techniques	Assessment (Effects, applicability, ...)
<b>CBAT for the abatement of air pollution</b>		
<b>a1</b>	Post combustion with air injection	Oxidation of carbon monoxide and metals
<b>a2</b>	Bag filter for final gas cleaning	Reduction of dust emissions and recovery of mixed oxide
<b>CBAT for the recycling of solid materials, waste prevention and the handling of waste</b>		
<b>s1</b>	Slag treatment	Slag is sold as construction material
<b>s2</b>	External processing of mixed oxide	Recovery of zinc and lead
<b>CBAT for the reduction of energy consumption</b>		
<b>h1</b>	Waste heat boiler	Heat recovery, steam generation

#### 4.2.5.3 Achieved emissions levels in fuming reactor plants

In Table 4-32, achieved emission levels and emissions load levels for a fuming reactor plant are listed.

**Table 4-32: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level <sup>*)</sup> [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t input]	Emission load level [g/t input]
Fuming reactor	Dust: 1 -5 Zn: 0.1 - 0.5 Pb: 0.1 Cd: < 0.001 SO <sub>2</sub> : < 800	30,000/7,500	Dust: 23 Zn: < 3 Pb: < 1 Cd: < 0.01 SO <sub>2</sub> : < 6,000

<sup>\*)</sup> To guarantee, that the *emission limit values* can be kept, the mentioned *emission level* has to be about 3 - 10 times lower than the *emission limit value*.

#### 4.2.6 Remelting plants

In the following, first a general characterisation of remelting plants is given. Then, the *specific* abatement techniques applied in German remelting plants are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

##### 4.2.6.1 Characterisation

A characterisation of the remelting process plants is given in Table 4-33.

**Table 4-33: Characterisation of the remelting process plants**

Criteria	Assessment
<b>Relevance</b>	For remelting of zinc scrap six major plants are in operation [49] in the EU. Due to the low energy consumption, remelting is the main process for recycling of zinc scrap.
<b>Flexibility concerning raw material use</b>	Old and new zinc scrap, foundry scrap as well as various secondary materials can be processed.
<b>Products</b>	Zinc Zinc alloys
<b>By-products</b>	Zinc ashes Hard zinc
<b>Environmental concerns:</b>	-

##### 4.2.6.2 CBAT for remelting plants

In Table 4-34 CBAT for remelting plants are summarised.

**Table 4-34: CBAT for remelting plants**

No.	Techniques	Assessment (Effects, applicability, ...)
	<b>CBAT for the abatement of air pollution</b>	
<b>a1</b>	Bag filter for off-gas cleaning	Removal of dust for recycling
	<b>CBAT for the reduction of water consumption and the control and treatment of waste water</b>	
<b>w1</b>	Cooling water circuit	Reduction of cooling water consumption
	<b>CBAT for the recycling of solid materials, waste prevention and the handling of waste</b>	
<b>s1</b>	Internal recycling of dusts, ashes and drosses	Recovery of metal content

##### 4.2.6.3 Achieved emissions levels in remelting plants

In Table 4-35, achieved emission levels and emissions load levels for remelting plants are listed.

**Table 4-35: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t zinc]	Emission load level [g/t zinc produced]
Melting furnace	Dust: 3.0 - 15.0 Zn: 1.5 - 7.5 Cd: < 0.001 - 0.01 Pb: 0.1 - 0.9	60,000 / 9,000 - 12,000	Dust: 25 - 90 Zn: 15 - 50 Cd: < 0.03 Pb: 2 - 8

Remelting plants can be operated effluent free.

#### 4.2.7 New-Jersey retort plants

In the following, first a general characterisation of the New-Jersey retort plant is given. In the following, the *specific* abatement techniques applied in the German New-Jersey retort plant are reviewed and finally, achieved emission levels and emission load levels are presented.

##### 4.2.7.1 Characterisation

A characterisation of the New-Jersey retort plants is given in Table 4-36.

**Table 4-36: Characterisation of the New-Jersey retort plants**

Criteria	Assessment
Relevance	Today, there is only one New-Jersey retort plants operated in the EU.
Flexibility concerning raw material use	A wide range of zinc bearing materials can be processed.
Products	Commercial zinc for further refining
By-products	Retort residue
Environmental concerns:	-

##### 4.2.7.2 Available techniques for the New-Jersey retort plants

In Table 4-37 applied in the New-Jersey retort plants are summarised.



**Table 4-37: Applied techniques in the New-Jersey retort plants**

No.	Techniques	Assessment (Effects, applicability, ... )
<b>Techniques for the abatement of air pollution</b>		
<b>a1</b>	Wet scrubbing and post combustion	Dedusting of process gas
<b>Techniques for the reduction of water consumption and the control and treatment of waste water</b>		
<b>w1</b>	Cooling water circuit	Reduction of cooling water use
<b>Techniques for the recycling of solid materials, waste prevention and the handling of waste</b>		
<b>s1</b>	Internal recycling zinc bearing sludge from gas cleaning	Recovery of zinc
<b>Techniques for the reduction of energy consumption</b>		
<b>h1</b>	Air preheating	Reduction of energy consumption
<b>h2</b>	Internal use of process gas	Reduction of energy consumption

#### 4.2.7.3 Achieved emissions levels in New-Jersey retort plants

In Table 4-38, achieved emission levels and emissions load levels for a New-Jersey retort plant are listed.

**Table 4-38: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t Zn]	Emission load level [g/t Zn]
New-Jersey retorts	Dust: 1.0 - 5.0 Zn: 0.5 - 2.0 Pb: 0.1 Cd: < 0.001	160,000 / 64,000	Dust: < 190 Zn: < 80 Pb: < 6 Cd: < 0.05

No water is discharged from the New-Jersey retort plant.



### 4.3 German Candidate BAT for lead production plants

Within the framework of integrated pollution prevention and control first of all the above-mentioned *general techniques and rules* as described in Chapter 4.1 should be considered for each plant operation. Additionally, for lead production plants several *process* as well as *plant specific* abatement techniques have proven their suitability for integrated pollution prevention and control. Techniques showing this potential have been considered as candidate BAT, too. In the following sections, the techniques applied in the German lead production industry are reviewed and a list of these candidates BAT (CBAT) is presented for each of the main production processes. The achieved emission levels and emission load levels are based on the following definitions:

#### ***Achieved emission level (air):***

This level gives the range of daily average emission values, determined on the basis of half-hour mean values<sup>22</sup>, of a contaminant in an off-gas flow [mg/Nm<sup>3</sup>]. Guidelines for the measurement of emission values are described in Section 4.1.8 and [4]. The given emission levels have been *achieved* in plants using the candidate best available techniques (described in this report in Chapter 3 and 4) over a long period of normal operation. It has to be mentioned, that the range of achieved emission levels based on daily average emission values is well below the *emission limit values* set in permits i.e. as half-hour mean values. Depending from process and abatement technologies the ratio between the given achieved emission levels and the set emission limit values in permits is up to 0.1.

#### ***Achieved emission load level (air):***

This value gives the product-specific *emission load* [g/t], calculated as a product of the *average annual emission value* of a contaminant [mg/Nm<sup>3</sup>], the average off-gas volume [Nm<sup>3</sup>/h] and the annual operation time [h/a], related to production capacity [t/a].

#### ***Achieved emission level (waste water):***

This level gives the range of average concentration values of a contaminant [mg/l] determined as 2 hours composite samples or as qualified random sample. Guidelines for the measurement of concentration values are described in Section 7.1.2.2 and [1]. The given emission levels have been *achieved* in plants using the candidate best available techniques (described in this report in Chapter 3 and 4) over a long period of normal operation. It has to be mentioned, that the range of achieved emission levels based on daily average emission values is well below the *emission limit values* set in permits i.e. as two hours composite samples or qualified

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<sup>22</sup> If a dust content is low, other measurement times and, consequently, other reference times may be necessary because of the limitation of detection (c.f. section 4.1.8).

random samples. Depending from process and abatement technologies the ratio between the given achieved emission levels and the set emission limit values in permits is up to 0.1.

***Achieved emission load level (waste water):***

This value gives the product-specific *emission load* [g/t], calculated as a product of the *average emission value* of a contaminant [mg/l], the average discharge volume [m<sup>3</sup>/h] and the annual operation time [h/a], related to production capacity [t/a].

An overview of the structure of Chapter 4.3 is given in Table 4-39.

**Table 4-39: Structure of Chapter 4.3 (overview)**

Main plants	Section	Characterisation	CBAT	Achieved emission level
QSL process (New direct smelting process)	4.3.1	4.3.1.1	Air (4.3.1.2) Water (4.3.1.3) Recycling/waste (4.3.1.4) Energy (4.3.1.5)	Air/water (4.3.1.6)
Sirosmelt process (New direct smelting process)	4.3.2	4.3.2.1	Air (4.3.2.2) Water (4.3.2.3) Recycling/waste (4.3.2.4) Energy (4.3.2.5)	Air/water (4.3.2.6)
<i>Imperial Smelting process</i>	<i>s. 4.2.2</i>	<i>s. 4.2.2.1</i>	<i>Air (s. 4.2.2.2) Water (s. 4.2.2.3) Recycling/waste (s.4.2.2.4) Energy (s.4.2.2.5)</i>	<i>Air/water (s. 4.2.2.6)</i>
Shaft furnace for battery recycling	4.3.3	4.3.3.1	Air (4.3.3.2) Water (4.3.3.3) Recycling/waste (4.3.3.4) Energy (4.3.3.5)	Air/water (4.3.3.6)
Rotary furnace a) Smelting of grid metal (Type A) b) Smelting of grid metal and desulphurised paste (Type B)	4.3.4	4.3.4.1	Air (4.3.4.2) Water (4.3.4.3) Recycling/waste (4.3.4.4) Energy (4.3.4.5)	Air/water (4.3.4.6)
Lead refining	4.3.5	4.3.5.1	Air - water - recycling/ waste - energy (4.3.5.2)	c.f. 4.3.1 / 4.3.2 / 4.3.3 / 4.3.4

### 4.3.1 QSL process plant

In the following, first a general characterisation of the QSL process plant is given. Then, the *specific* abatement techniques applied in German QSL plant are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

#### 4.3.1.1 Characterisation

A characterisation of the QSL plant is given in Table 4-40.

**Table 4-40: Characterisation of the QSL plant**

Criteria	Assessment
<b>Relevance</b>	The QSL process is a modern bath smelting process running on a technical scale since years. The process demonstrates the advantages of the new direct smelting processes (e.g. use of the chemical energy of the inputs, high direct lead bullion yield, lower off-gas volume etc.).
<b>Flexibility concerning raw material use</b>	Wide range of primary and secondary materials can be processed: - dry/wet fine and lumpy materials - sulphur and cadmium containing materials
<b>Products</b>	Lead bullion for further refining Sulphuric acid
<b>By-products</b>	Iron-silicate slag Calomel
<b>Environmental concerns:</b> Waste generation Utilisation of by-products	Sludge from waste water treatment Zinc-cadmium carbonate Slag reduction/slag quality

#### 4.3.1.2 CBAT for the abatement of air pollution

In Table 4-41 CBAT for the abatement of air pollution from QSL plants are summarised.

**Table 4-41: CBAT for the abatement of air pollution**

No.	Abatement techniques	Assessment (Effects, applicability, ...)
<b>Process unit(s): Raw materials/handling/preparation</b>		
<b>a1</b>	Hoods	Capturing of emissions, prevention of fugitive emissions
<b>a2</b>	Bag filters	Off-gas dedusting
<b>Process unit(s): QSL reactor/Gas cleaning system</b>		
<b>b1</b>	Process gas cleaning with cooling, hot ESP and wet ESP	Off-gas dedusting
<b>b2</b>	Further off-gas cleaning (Boliden/Norzink process)	Precipitation of gaseous mercury
<b>b3</b>	Further off-gas processing in a sulphuric acid plant	Recovery of sulphur
<b>b4</b>	Hoods and complete enclosure of the lead bullion/slag outlet	Collection of emissions, prevention of fugitive emissions
<b>b5</b>	Bag filter for exhaust gas cleaning	Final gas cleaning
<b>Process unit(s): Sulphuric acid plant</b>		
<b>d1</b>	Double absorption contact plant	Conversion of SO <sub>2</sub> with an efficiency of more than 99.6%
<b>Process unit(s): Slag treatment</b>		
<b>d1</b>	Hoods	Capturing of emissions, prevention of fugitive emissions
<b>d2</b>	Wet ESP	Final gas cleaning
<b>Process unit(s): Cadmium leaching plant</b>		
<b>e1</b>	Acidic leaching	Leaching of Cadmium and Chlorides to limit a recirculation to the process
<b>Process unit(s): Refinery</b>		
<b>Lead refining plant (c.f. 4.3.5)</b>		

#### 4.3.1.3 CBAT for the reduction of water consumption and the control and treatment of waste water

In Table 4-42 CBAT for the reduction of water consumption and the control and treatment of waste water are summarised.

**Table 4-42: CBAT for reduction of water consumption and treatment of waste water**

No.	Techniques	Assessment (Effects, applicability, ...)
<b>w1</b>	Use of a central waste water treatment plant	The water treatment scheme is described in 4.1.
<b>w2</b>	Internal use of process water	Reduction of fresh water consumption and effluent generation
<b>w3</b>	Recirculation of cooling water	Reduction of fresh water consumption

#### 4.3.1.4 CBAT for the recycling of solid materials, waste prevention and the handling of waste

In Table 4-43 main techniques for the recycling of solid materials, waste prevention and the handling of waste are summarised.

**Table 4-43: CBAT for the recycling of solid materials, waste prevention and handling of waste**

No.	Techniques	Assessment (Effects, applicability, ...)
s1	Granulation of slag	Granulated slag can be used in different options
s2	Leaching of flue dusts	Precipitation of cadmium and recovery as cadmium carbonate
s3	Internal recirculation of the leaching residue	Recovery of lead
s4	Decopperizing of lead bullion	Separation of copper for later recovery
s5	Recovery of mercury from roast gas	Production of Calomel, but the market for Calomel is limited

#### 4.3.1.5 CBAT for the reduction of energy consumption

In Table 4-44 CBAT for the reduction of energy consumption are summarised.

**Table 4-44: CBAT for the reduction of energy consumption and heat recovery**

No.	Techniques	Assessment (Effects, applicability, ...)
h1	Waste heat boiler for heat recovery from the furnace off-gas	Steam generation
h2	Generation of electrical energy	Electrical energy is used for internal plant consumption.

#### 4.3.1.6 Achieved emissions levels in QSL process plants

In Table 4-45, achieved emission levels and emissions load levels for the German QSL plant are listed.

**Table 4-45: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t Pb]	Emission load level [g/t Pb]
Raw material storage, handling, refinery	Dust: 1 - 2 Pb: 0.2 - 1 Cd: 0.005 - 0.05 NO <sub>x</sub> : 10 - 20 <sup>*)</sup> SO <sub>2</sub> : 5 - 200 <sup>*)</sup>	220,000 / 20,000	Dust: 20 - 40 Pb: 4 - 20 Cd: 0.1 - 1 NO <sub>x</sub> : 200 - 400 <sup>*)</sup> SO <sub>2</sub> : < 600 <sup>*)</sup>
Sulphuric acid plant	Dust: < 1 Pb: 0.001 - 0.02 Cd: 0.001 - 0.002 NO <sub>x</sub> : 250 - 400 SO <sub>2</sub> : 200 - 300	20,000 / 1,900	Dust: < 2 Pb: < 0.1 Cd: < 0.01 NO <sub>x</sub> : 500 - 750 SO <sub>2</sub> : 400 - 600 SO <sub>3</sub> : 200
Slag granulation	Dust: 1 - 5 Pb: 0.5 - 2 Cd: < 0.001 NO <sub>x</sub> : < 10 SO <sub>2</sub> : < 20	190 / 20	Dust: 0.02 - 0.1 Pb: traces Cd: traces NO <sub>x</sub> : < 0.2 SO <sub>2</sub> : traces

<sup>\*)</sup> The SO<sub>2</sub> and NO<sub>x</sub> emissions arise during the refining operations.

In Table 4-46, achieved emissions levels for waste water discharges are summarised. A typical of a QSL plant is about 10 m<sup>3</sup>/h.

**Table 4-46: Achieved emission levels for waste water discharges**

Element	Emission level [mg/l]	Load level [g/t lead]	Element	Emission level [mg/l]	Load level [g/t lead]
Cu	0.01	< 0.01	As	< 0.05	< 0.05
Pb	0.2	< 0.18	Ni	< 0.05	< 0.05
Zn	0.3	< 0.27	Cr	< 0.05	< 0.05
Cd	< 0.05	< 0.05	Sulphide	< 0.1	< 0.09
Hg	< 0.001	< 0.001	AOX	< 0.1	< 0.09



### 4.3.2 Sirosmelt plant

#### 4.3.2.1 Characterisation

A characterisation of the Sirosmelt plant is given in Table 4-47.

**Table 4-47: Characterisation of the Sirosmelt plant**

Criteria	Assessment
<b>Relevance</b>	Since the beginning of the second quarter 1996, one Sirosmelt plant is operating in Germany on a technical scale. The process demonstrates the advantages of the new direct smelting processes (e.g. use of the chemical energy of the inputs, high direct lead bullion yield, lower off-gas volume etc.).
<b>Flexibility concerning raw materials</b>	A wide range of primary and secondary dry or wet material in fine or defined lumpy form can be processed.
<b>Products</b>	Lead bullion for further refining Sulphuric acid
<b>By-products</b>	Granulated slag as iron silicate slag. Mercury residue for recycling in another smelter
<b>Environmental concerns:</b> Utilisation of by-products Waste generation	Slag reduction Sludges from waste water treatment

#### 4.3.2.2 CBAT for the abatement of air pollution

In Table 4-48 CBAT for the abatement of air pollution from the Sirosmelt plant are summarised.

**Table 4-48: CBAT for the abatement of air pollution**

No.	Abatement techniques	Assessment (Effects, applicability, ...)
<b>Process unit(s): Raw materials/handling/preparation</b>		
<b>a1</b>	Total enclosed storage, hoods, closed conveyors	Capturing of emissions, prevention of fugitive emissions
<b>a2</b>	Bag filters	Off-gas dedusting
<b>Process unit(s): QSL reactor/Gas cleaning system</b>		
<b>b1</b>	Process gas cleaning with cooling, hot ESP and wet ESP	Off-gas dedusting
<b>b2</b>	Further off-gas cleaning (Boliden/Norzink process)	Recovery of sulphur
<b>b3</b>	Further off-gas processing in a sulphuric acid plant	Capturing of emissions, prevention of fugitive emissions
<b>b4</b>	Hoods and complete enclosure of the lead bullion/slag outlet	Final off-gas cleaning
<b>b5</b>	High vacuum dedusting unit	Prevention of fugitive emissions
<b>Process unit(s): Sulphuric acid plant</b>		
<b>d1</b>	Double absorption contact plant	Conversion of SO <sub>2</sub> with an efficiency of more than 99.6%
<b>d2</b>	<i>Boliden Chemie Process</i> for mercury removal	Precipitation of mercury
<b>Process unit(s): Slag treatment</b>		
<b>d1</b>	Hoods	Capturing of emissions, prevention of fugitive emissions
<b>d2</b>	Wet ESP	Final gas cleaning
<b>Process unit(s): Cadmium leaching plant</b>		
<b>e1</b>	Acidic leaching	Separation of Chlorine and Cadmium and precipitation of CdCO <sub>3</sub>
<b>Process unit(s): Refinery</b>		
<b>Lead refining plant (c.f. 4.3.5)</b>		

#### 4.3.2.3 CBAT for the reduction of water consumption and the control and treatment of waste water

In Table 4-49 CBAT for the reduction of water consumption and the control and treatment of waste water are summarised.

**Table 4-49: CBAT for the reduction of water consumption and treatment of waste water**

No.	Techniques	Assessment (Effects, applicability, ...)
<b>w1</b>	Waste water treatment in a central waste water treatment plant	The water treatment scheme is described in 4.1.
<b>w2</b>	Internal use of rain and process water	Reduction of fresh water consumption and waste water
<b>w3</b>	Recirculation of cooling water	Reduction of cooling water and energy input to the river

#### 4.3.2.4 CBAT for the recycling of solid materials, waste prevention and the handling of waste

In Table 4-50 CBAT for the recycling of solid materials, waste prevention and the handling of waste are summarised.

**Table 4-50: CBAT for the recycling of solid materials, waste prevention and handling of waste**

No.	Techniques	Assessment (Effects, applicability, ...)
s1	Granulation of slag	Granulated slag can be used in different options
s2	Internal recirculation of the main part of the flue dust	Recovery of lead
s3	Internal leaching of remaining flue dust	Separation of chlorine and cadmium and precipitation of cadmium carbonate
s4	Internal recirculation of leaching residue	Recovery of lead
s5	Decopperizing of lead bullion	Recovery of copper bearing products for further treatment
s6	Recovery of mercury from sulphuric acid	Production of mercury sludge for further treatment and Calomel production in the zinc plant

#### 4.3.2.5 CBAT for the reduction of energy consumption

In Table 4-51 CBAT for the reduction of energy consumption are summarised.

**Table 4-51: CBAT for the reduction of energy consumption and heat recovery**

No.	Techniques	Assessment (Effects, applicability, ...)
h1	Waste heat boiler for heat recovery of heat from furnace off-gas	Steam generation for heating and supplying of drives
h2	Oxygen enrichment of blast	Energy reduction for smelting

#### 4.3.2.6 Achieved emissions levels in the Sirosmelt plant

In Table 4-52, emission levels and emissions load levels which are achieved in the actual realisation stage of the Sirosmelt plant are listed.

**Table 4-52: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level <sup>*)</sup> [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t Pb]	Emission load level [g/t Pb]
Raw material storage / handling	Dust: 0.002 - 0.068 Pb: < 0.001 - 0.030 Cd: << 0.001	118,000 / 10,500	Dust: 0.14 Pb: 0.05 Cd: < 0.001
Sulphuric acid plant	NO <sub>x</sub> : 2.5 - 15.0 SO <sub>2</sub> : 300 - 700	35,000 / 3,100	NO <sub>x</sub> : 30 SO <sub>2</sub> : 1,560
Slag granulation / furnace area / decopperizing	Dust: 0.18 - 3.6 Pb: 0.1 - 2.2 Cd: << 0.001 - 0.017 SO <sub>2</sub> : 40 - 600	110,000 / 9,800	Dust: 9.6 Pb: 5.9 Cd: 0.03 SO <sub>2</sub> : 3,150
Refinery (c.f. 4.3.5)	Dust: 0.001 - 0.15 Pb: < 0.001 - 0.11 Cd: Traces NO <sub>x</sub> : Traces	66,000 / 5,900	Dust: 0.3 Pb: 0.1 Cd: << 0.001 NO <sub>x</sub> : Traces

<sup>\*)</sup> To guarantee, that the emission limit values can be kept, the mentioned emission level has to be about 3 - 10 times lower than the emission limit value.

In Table 4-53, achieved emissions levels for waste water discharges are summarised.

**Table 4-53: Achieved emission levels for waste water discharges**

Element	Emission level <sup>*)</sup> [mg/l]	Load level [g/t lead]	Element	Emission level <sup>*)</sup> [mg/l]	Load level [g/t lead]
Cu	n. a.	n. a.	As	< 0.001 - 0.1	< 0.03
Pb	0.01 - 0.5	< 0.02	Ni	n. a.	n. a.
Zn	0.01 - 0.4	< 0.04	Cr	n. a.	n. a.
Cd	< 0.005	< 0.001	Sulphide	< 0.001 - 0.01	< 0.01
Hg	< 0.001	< 0.001	AOX	0.004 - 0.13	< 0.04

<sup>\*)</sup> To guarantee, that the emission limit values can be kept, the mentioned emission level has to be about 10 times lower than the emission limit value (c.f. Chapter 4.3 ).

### 4.3.3 Shaft furnace plants for battery recycling

In the following, first a general characterisation of the shaft furnace plant for battery recycling is given. Then, the *specific* abatement techniques applied in the German shaft furnace plant are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

#### 4.3.3.1 Characterisation

A characterisation of the shaft furnace process plants is given in Table 4-54.

**Table 4-54: Characterisation of the shaft furnace process plants**

Criteria	Assessment
<b>Relevance</b>	About 4 plants are operated in the EU.
<b>Flexibility concerning raw material use</b>	Battery scrap is the main input material; to a certain extent other lead bearing materials can be processed.
<b>Products</b>	Lead bullion for further refining
<b>By-products</b>	Iron silicate slag Iron/lead matte
<b>Environmental concerns:</b> Waste generation Emissions into the atmosphere	Flue dusts with high chlorine content Control of SO <sub>2</sub> -emissions in the furnace off-gas

#### 4.3.3.2 CBAT for the abatement of air pollution

In Table 4-55 CBAT for the abatement of air pollution from shaft furnace plants are summarised.

**Table 4-55: CBAT for the abatement of air pollution**

No.	Techniques	Assessment (Effects, applicability, ...)
<b>Process unit(s): Raw materials handling</b>		
<b>a1</b>	Moistening of raw materials	Prevention of fugitive emissions
<b>a2</b>	Indoor storage or storage under a roof	Prevention of fugitive emissions
<b>a3</b>	Removal of parts of the waste acid	Reduction of sulphur content of the inputs
<b>Process unit(s): Shaft furnace/gas cleaning</b>		
<b>b1</b>	Secondary hoods at the tapping area	Collection of fugitive emissions
<b>b2</b>	Gas cleaning system with post combustion chamber (minimum: 850°C, typically: 1,100°C), dry quenching with secondary off-gases fabric filter	Removal of hydrocarbons and dust
<b>b3</b>	Oxygen enrichment of process air	Reduction of off-gas volume and generation of flue dusts
<b>b4</b>	Injection of calcium hydroxide, if necessary	Prevention of sulphur dioxide emissions peaks
<b>Process unit(s): Refinery</b>		
<b>Lead refining plant (c.f. 4.3.5)</b>		

#### 4.3.3.3 CBAT for the reduction of water consumption and the control and treatment of waste water

In Table 4-56 CBAT for the reduction of water consumption and the control and treatment of waste water are summarised.

**Table 4-56: CBAT for the reduction of water consumption and treatment of waste water**

No.	Techniques	Assessment (Effects, applicability, ...)
<b>w1</b>	Adequate waste water treatment	The water treatment scheme is described in 4.1.
<b>w2</b>	Internal use of treated water	Reduction of fresh water consumption and effluent generation
<b>w3</b>	Recirculation of shaft furnace cooling water	Reduction of fresh water consumption

#### 4.3.3.4 CBAT for the recycling of solid materials, waste prevention and the handling of waste

In Table 4-57 main techniques for the recycling of solid materials and the prevention of waste are summarised.

**Table 4-57: CBAT for the recycling of solid materials, waste prevention and handling of waste**

No.	Techniques	Assessment (Effects, applicability, ...)
s1	Separation, collection, treatment and re-use of waste acid	Waste acid can be used as a substitute for virgin acid in various applications, if a market exist.
s2	External treatment of matte	Recovery of sulphur, lead and copper
s3	External leaching of shaft furnace dust	Removal of chlorides and production of lead carbonate
s4	Internal recycling of lead carbonate	Recovery of lead
s5	Internal recycling of shaft furnace slag as return slag	The return of slag is necessary to get the adequate porosity of the material column
s6	External use of remaining shaft furnace slag	Used a secondary construction material, where ever possible
s7	Use of refining dross (internal/external)	Recovery of lead and other metals

#### 4.3.3.5 CBAT for the reduction of energy consumption

In Table 4-58 main techniques for the reduction of energy consumption are summarised.

**Table 4-58: CBAT for the reduction of energy consumption and heat recovery**

No.	Techniques	Assessment (Effects, applicability, ...)
h1	Oxygen enrichment of process air	Increase in energy efficiency

#### 4.3.3.6 Achieved emissions levels in shaft furnace plants for battery recycling

In Table 4-59, achieved emission levels and emissions load levels for shaft furnace plants are listed.

**Table 4-59: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level <sup>*)</sup> [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t Pb] <sup>1)</sup>	Emission load level [g/t Pb] <sup>1)</sup>
Shaft furnace gas cleaning / refinery	Dust: 0.2 - 2.0 Pb: 0.1 - 1.0 Cd: 0.002 - 0.05 NO <sub>x</sub> : 20 - 150 SO <sub>2</sub> : 300 - 800	60,000 / 16,000	Dust: < 7 Pb: < 4 Cd: < 0.08 NO <sub>x</sub> : < 600 SO <sub>2</sub> : < 9,000

<sup>\*)</sup> To guarantee, that the *emission limit values* can be kept, the mentioned *emission level* has to be about 3 - 10 times lower than the *emission limit value*.

In Table 4-60, achieved emissions levels for waste water discharges from shaft furnace plants are summarised. A typical shaft furnace plant has a waste water flow of about 2 m<sup>3</sup>/h.

**Table 4-60: Achieved emission levels for waste water discharges**

Element	Emission level <sup>*)</sup> [mg/l]	Load level [g/t lead]	Element	Emission level <sup>*)</sup> [mg/l]	Load level [g/t lead]
Cu	0.01 - 0.05	< 0.01	As	0.001 - 0.01	< 0.001
Pb	0.05 - 0.5	< 0.08	Ni	0.02 - 0.2	< 0.05
Zn	0.05 - 0.8	< 0.10	Cr	0.005 - 0.05	< 0.006
Cd	0.01 - 0.15	< 0.05	Sulphide	0.005 - 0.1	< 0.006
Hg	< 0.001	<< 0.001			

<sup>\*)</sup> To guarantee, that the emission limit values can be kept, the mentioned emission level has to be about 10 times lower than the emission limit value (c.f. Chapter 4.3).



#### 4.3.4 Rotary furnace plants (MA or CX technology)

As the use of modern separation technologies avoids the burning of plastics (PVC, ebonite) and allows a recovery of polypropylene, only rotary furnace applying these techniques (MA or CX technology) are investigated further. Furthermore, the following processing types for rotary furnace plants have to be distinguished:

- a) Smelting of grid metal / external treatment of paste (**type A**)
- b) Paste desulphurisation / smelting of grid metal and paste / sodium sulphate production (**type B**)

In the following, first a general characterisation of the rotary furnace plants is given. Then, the *specific* abatement techniques applied in German rotary furnace plants are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

##### 4.3.4.1 Characterisation

A characterisation of the rotary furnace plants (MA or CX technology) is given in Table 4-61.

**Table 4-61: Characterisation of the rotary furnace plants (MA or CX technology)**

Criteria	Assessment	
<b>Relevance</b>	The short rotary furnace is the most often used device for secondary lead production in the EU. Modern plant technology allows the recovery of polypropylene; the separated paste can be processed externally (type A) or internally (type B).	
<b>Flexibility concerning raw material use</b>	Besides battery scrap as main input material, other lead bearing secondary materials are processed.	
<b>Products</b>	<b>Type A:</b> Lead bullion for further refining Polypropylene	<b>Type B:</b> Lead bullion for further refining Polypropylene Sodium sulphate
<b>By-products</b>	Paste	
<b>Environmental concerns:</b> Waste generation	Slag Plastic waste	Slag Plastic waste

##### 4.3.4.2 CBAT for the abatement of air pollution

In Table 4-62 CBAT for the abatement of air pollution from rotary furnace plants (MA or CX technology) are summarised.

**Table 4-62: CBAT for the abatement of air pollution**

No.	Techniques	Assessment (Effects, applicability, ...)
<b>Process unit(s): Raw materials handling/battery treatment</b>		
<b>a1</b>	Indoor storage or storage under a roof ( <b>Type A+B</b> )	Prevention of fugitive emissions
<b>Process unit(s): Rotary furnace/gas cleaning system</b>		
<b>b1</b>	Furnace encapsulation ( <b>Type A+B</b> )	Prevention of emissions
<b>b2</b>	Fabric filter for off-gas cleaning ( <b>Type A+B</b> )	Dedusting
<b>Process unit(s): Refinery</b>		
<b>Lead refining plant (c.f. 4.3.5)</b>		

#### 4.3.4.3 CBAT for the reduction of water consumption and the control and treatment of waste water

In Table 4-63 CBAT for the reduction of water consumption and the control and treatment of waste water are summarised.

**Table 4-63: CBAT for the reduction of water consumption and treatment of waste water**

No.	Techniques	Assessment (Effects, applicability, ...)
<b>w1</b>	Adequate waste water treatment ( <b>Type A+B</b> )	The water treatment scheme is described in 4.1.
<b>w2</b>	Recirculation of process water from hydroseparation ( <b>Type A+B</b> )	Reduction of fresh water consumption

#### 4.3.4.4 CBAT for the recycling of solid materials, waste prevention and the handling of waste

In Table 4-64 main techniques for the recycling of solid materials, waste prevention and the handling of waste are summarised.

**Table 4-64: CBAT for the recycling of solid materials, waste prevention and handling of waste**

No.	Techniques	Assessment (Effects, applicability, ...)
s1	Separation of ebonite, PVC and polypropylene (Type A + B)	Recovery of polypropylene chips as by-product Use of residual for energy recovery Prevention of chloride input from PVC to the metallurgical process Prevention of sulphur input from ebonite to the metallurgical process
s2	Collection and (internal) treatment of waste acid (Type A + B)	-
s3	Agglomeration and recycling of flue dust (Type A + B)	Minimisation of dust handling Internal treatment for lead recovery
s4	Compoundation of polypropylene (Type A + B)	Production of a marketable product
s5	Desulphurisation of paste (Type B)	Production of water free sodium sulphate as by-product Internal recycling of desulphurised paste
s6	External recycling of battery paste (Type A)	Recovery of lead and sulphur if the paste is processed in a modern lead smelting plant
s7	Internal recycling of sludges from waste water treatment (Type A + B)	Recovery of lead

#### 4.3.4.5 CBAT for the reduction of energy consumption

In Table 4-65 main techniques for the reduction of energy consumption are summarised.

**Table 4-65: CBAT for the reduction of energy consumption and heat recovery**

No.	Techniques	Assessment (Effects, applicability, ...)
h1	Separation of plastic materials (Type A + B)	Recovery of polypropylene with an energetic value of 3,000 MJ/t Pb Recovery of other plastics with an energetic value of 3,000 MJ/t Pb
h2	Waste heat recovery (furnace off-gas) (Type A+B)	Steam generation for internal use

#### 4.3.4.6 Achieved emissions levels in rotary furnace plants (MA or CX technology)

In Table 4-66, achieved emission levels and emissions load levels for both types of rotary furnace plants are listed.

**Table 4-66: Achieved emission levels for controlled emissions into the atmosphere (main sources)**

Process unit	Emission level [mg/Nm <sup>3</sup> ]	Off-gas volume [Nm <sup>3</sup> /h] / [Nm <sup>3</sup> /t Pb] <sup>*)</sup>	Emission load level [g/t Pb] <sup>*)</sup>
Rotary furnace (Type A + B) / refinery	Dust: 0.5 - 4 Pb: 0.2 - 1 Cd < 0.005 NO <sub>x</sub> : 5 - 20 SO <sub>2</sub> : 50 - 150	150,000 - 250,000 / 30,000 - 45,000	Dust: 15 - 80 Pb: 5 - 25 Cd < 0.2 NO <sub>x</sub> : 200 - 500 SO <sub>2</sub> : 2,500 - 4,000

<sup>\*)</sup> per tonne lead / lead bullion produced

In Table 4-67, achieved emissions levels for waste water discharges from rotary furnace plants are summarised. The given values are valid for both types of plants. The range for typical discharge flows is 12.5 - 25 m<sup>3</sup>/h (or 3.5 - 4.5 m<sup>3</sup>/t Pb).

**Table 4-67: Achieved emission levels for waste water discharges**

Element	Emission level [mg/l]	Load level [g/t Pb]	Element	Emission level [mg/l]	Load level [g/t Pb]
Cu	0.01	< 0.05	As	0.07	< 0.3
Pb	0.12 - 0.2	0.4 - 0.7	Ni	< 0.1	< 0.4
Zn	0.2	< 0.7	Cr	< 0.05	< 0.2
Cd	0.05	< 0.2	Sulphide	< 0.2	< 0.7
Hg	< 0.001	<< 0.01	AOX	0.06 - 0.2	0.2 - 0.7

### 4.3.5 Lead refining plants

In the following, first a general characterisation of lead refining plants is given. Then, the *specific* abatement techniques applied in German lead refineries are reviewed to present a list of techniques, which have to be considered as CBAT for each of the environmental media. Finally, achieved emission levels and emission load levels are presented.

#### 4.3.5.1 Characterisation

A characterisation of the lead refining plants is given in Table 4-68.

**Table 4-68: Characterisation of the lead refining plants**

Criteria	Assessment
<b>Relevance</b>	Lead refining is necessary for the production of marketable lead alloys and soft lead quantities
<b>Flexibility concerning raw material use</b>	The selection of raw materials depends on the product specifications and the refining equipment of the individual plant.
<b>Products</b>	Refined lead Lead alloys (e.g. PbSb, PbCa, PbSn, ...)
<b>By-products</b>	Drosses, skimmings, silver/bismuth crusts, ...
<b>Environmental concerns:</b>	-

#### 4.3.5.2 CBAT for lead refining plants

In Table 4-69 CBAT for lead refining plants are summarised.

**Table 4-69: CBAT for lead refining plants**

No.	Techniques	Assessment (Effects, applicability, ...)
	<b>CBAT for the abatement of air pollution</b>	
<b>a1</b>	Ventilation/hood system for refining kettles	Capturing of emissions
<b>a2</b>	Fabric filters for exhaust gas cleaning	Dedusting
<b>a3</b>	Skimming machines for removal of drosses and slags	Prevention of fugitive emissions
	<b>CBAT for the recycling of solid materials, waste prevention and the handling of waste</b>	
<b>s1</b>	Internal or external recycling of dross, crusts	Waste minimisation and metal recovery

Achieved emission levels and emissions load levels for lead refining plants have already been included in the different sections of Chapter 4.3 dealing with the production process plants.

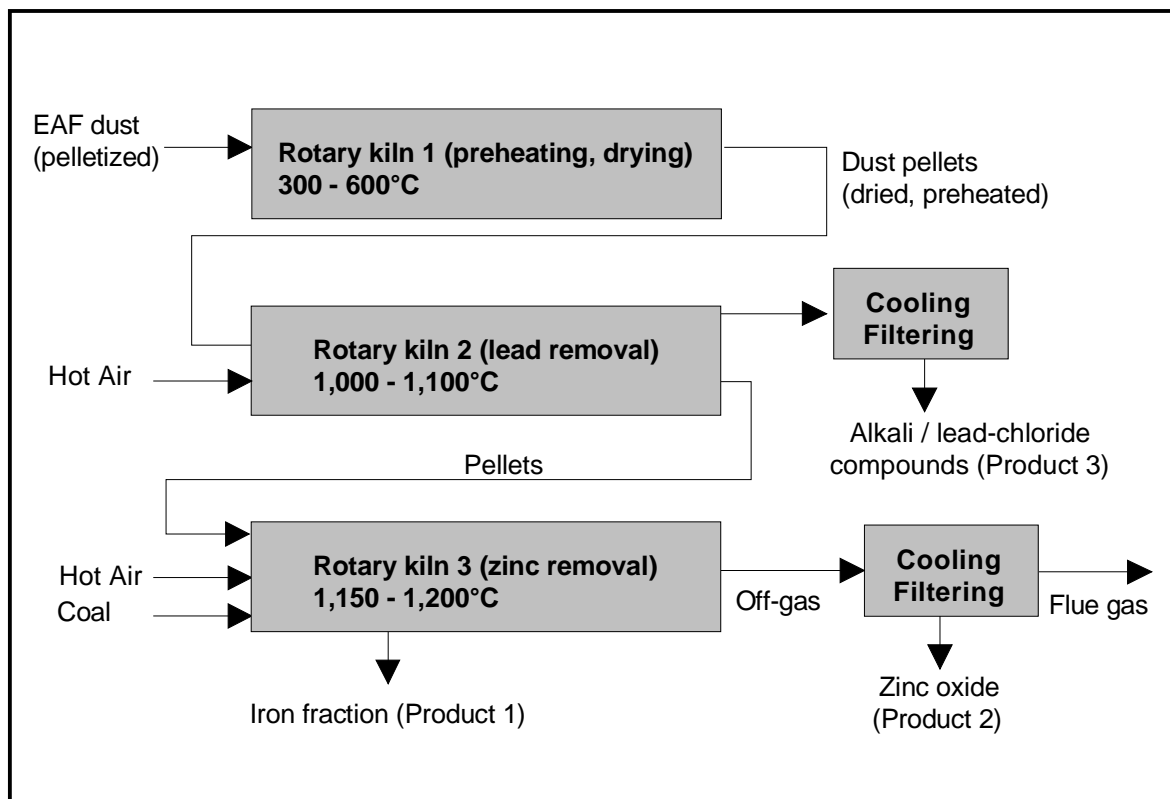


## 5 Emerging techniques, future trends

In this chapter, a collection of so-called emerging techniques and future trends is presented. According to the discussions with the national experts, the described processes may be seen as relevant for the further development in Germany.

### *BSN process for the recycling of EAF-dusts<sup>23</sup>*

The BSN process can be used for recovery of zinc and lead from metallurgical-works dust. A schematic view of the process is shown in figure 6-1. BSN GmbH plans to erect a 25,000 t/a plant, using the self developed BSN process, for the treatment of its EAF dusts. Main components of this plant are three rotary kilns operated within different temperature intervals (300 - 600°C, 1,000 - 1,100°C, 1,150 - 1,200°C). Products of this residue free process are zinc oxide, alkali/lead-chloride, and iron pellets.



**Figure 5-1: Schematic view of the BSN process for treatment of EAF dusts**

Source: following Klein et al. [39]

The operation of an industrial processing plant with a capacity of 8,000 t/a has started in November 1998.

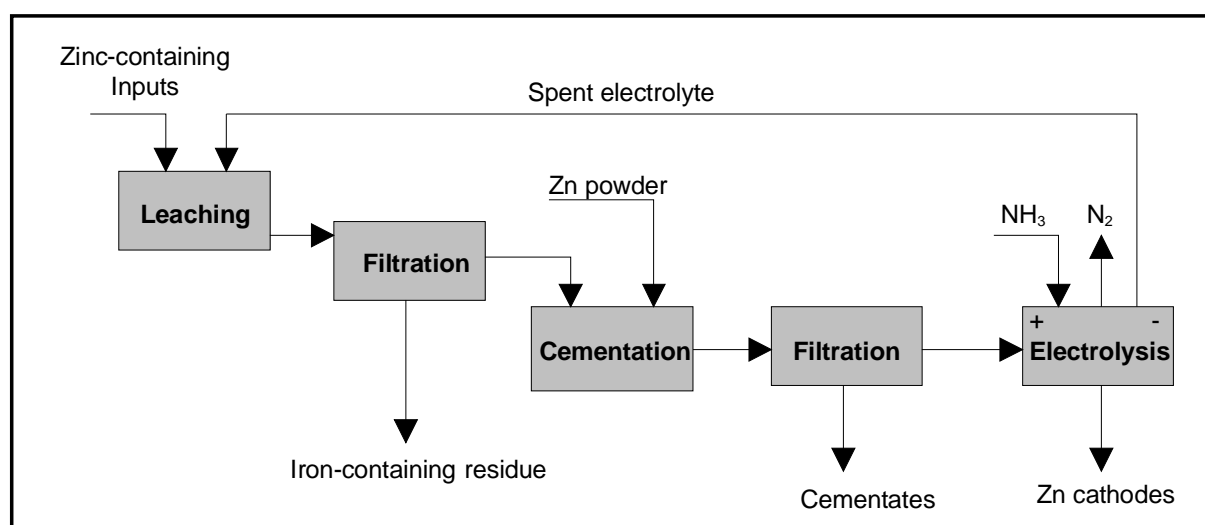
<sup>23</sup> Badische Stahl-Nebenprodukte GmbH, Kehl (Germany)

### ***EZINEX process for the treatment of secondary zinc-containing materials***

The EZINEX process has been developed for the on-site recovery of zinc from EAF-dusts. In Udine (Italy), the first plant on an industrial scale is in operation. It has a treatment capacity of 12,000 t/a resulting in an annual production of 2,000 t zinc cathodes [64]. The main aggregates are the leaching tanks, the filter, the cementation tanks, and the electrolysis cells.

In the first process step, the zinc containing inputs are fed to the leaching reactor and dissolved in spent electrolyte based on ammonium and alkali chloride. Besides iron most of the heavy metals are dissolved in form of their ammine complexes. The remaining residue containing iron oxides, zinc ferrite and silica is separated by press-filtration and dried. After pelletisation with coke, it can be recycled, for example to the EAF. The solution is further purified by cementation of copper, lead and cadmium under addition of zinc powder. The recovered precipitate is sent to a lead smelting plant for further recycling. The purified solution is led to the electrolysis cells where zinc is reduced by means of titanium cathodes. The formation of  $\text{Cl}_2$  at the graphite anodes can be avoided because of the reaction of chlorine with  $\text{NH}_4\text{OH}$  to  $\text{HCl}$  and nitrogen. As a consequence, an equivalent amount of  $\text{NH}_3$  is added to the electrolysis cells. In case of an insufficient purification other heavy metals are co-deposited. During the leaching step alkali chlorides, fluorides and most of the sulphates are dissolved, too. To avoid an accumulation of these substances, a share of the electrolyte has to be evaporated for the crystallisation of chlorides and sulphates.

According to [47], the EZINEX process may be more suited for the treatment of secondary materials with a higher zinc content than EAF-dust, which are not usable for conventional zinc electrolysis plants. As a consequence, the amount of residues, which is produced in the EZINEX process, can be reduced. A schematic flowsheet of the modified EZINEX process is shown in Figure 5-2.



**Figure 5-2: Schematic flowsheet of the EZINEX process**



## 6 References

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## 7 Annex

### 7.1 Definitions

In the following, some definitions are given to clarify the figures and statements in this report:

- **Achieved emission level (air):**

This level gives the range of daily average emission values, determined on the basis of half-hour mean values<sup>24</sup>, of a contaminant in an off-gas flow [mg/Nm<sup>3</sup>]. Guidelines for the measurement of emission values are described in Section 4.1.8 and [4]. The given emission levels have been *achieved* in plants using the candidate best available techniques (described in this report in Chapter 3 and 4) over a long period of normal operation. It has to be mentioned, that the range of achieved emission levels based on daily average emission values is well below the emission limit values set in permits i.e. as half-hour mean values. Depending from process and abatement technologies the ratio between the given achieved emission levels and the set emission limit values in permits is up to 0.1.

- **Achieved emission load level (air):**

This value gives the product-specific *emission load* [g/t], calculated as a product of the *average annual emission value* of a contaminant [mg/Nm<sup>3</sup>], the average off-gas volume [Nm<sup>3</sup>/h] and the annual operation time [h/a], related to production capacity [t/a].

- **Achieved emission level (waste water):**

This level gives the range of average concentration values of a contaminant [mg/l] determined as 2 hours composite samples or as qualified random sample. Guidelines for the measurement of concentration values are described in Section 7.1.2.2 and [1]. The given emission levels have been *achieved* in plants using the candidate best available techniques (described in this report in Chapter 3 and 4) over a long period of normal operation. It has to be mentioned, that the range of achieved emission levels based on daily average emission values is well below the emission limit values set in permits i.e. as two hours composite samples or qualified random samples. Depending from process and abatement technologies the ratio between the given achieved emission levels and the set emission limit values in permits is up to 0.1.

- **Achieved emission load level (waste water):**

This value gives the product-specific *emission load* [g/t], calculated as a product of the *average emission value* of a contaminant [mg/l], the average discharge volume [m<sup>3</sup>/h] and the annual operation time [h/a], related to production capacity [t/a].

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<sup>24</sup> If a dust content is low, other measurement times and, consequently, other reference times may be necessary because of the limitation of detection (c.f. section 4.1.8).





## **7.2 Information on current legislation relevant to the zinc and lead production industry**

### **7.2.1 Introduction**

Various regulations concerning environmental standards have to be complied with related to the erection and operation of non-ferrous metal production plants, since zinc and lead production industry is a consumer of energy and a potential source of air and water pollution as well as solid wastes. Consequently, the immediate environmental concerns are the usage of energy, control of air pollution (particularly CO, SO<sub>x</sub>, NO<sub>x</sub> and heavy metals), solid waste disposal and recycling, waste water emissions and - more recently with the increased amounts of recycled contaminated scrap metals - also harmful organic emissions. Existing regulations lay down general standards for

- the use of raw materials,
- energy consumption and the usage of waste heat,
- air quality,
- water quality,
- waste management and disposal of hazardous materials, and
- noise quality, vibration, smell.

Since this report deals only with the German zinc and lead production, the following sections give a brief overview of the current German legislation for zinc and lead production plants. In addition, a rough overview of important regulations on an international level is given. Legislation on a European level is excluded.

### **7.2.2 Regulations on a German level<sup>25</sup>**

Important regulations relevant for non-ferrous metal production plants in Germany are laid down in the BImSchG (Federal Immission Control Act), the WHG (Federal Water Act) and the KrW-/AbfG (Federal Recycling and Waste Management Act). Germany uses a segregated media permitting system for different environmental media, but the final decision on an application is reached by the assessment of environmental impacts on all media by the local authorities. Also noise requirements are considered in the licensing procedure. Germany aims at favouring pollution prevention in the licensing procedure. The "precautionary principle" has a legal status which permits the setting of standards. Legal standards are not subject to any negotiation in the licensing procedure in Germany.

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<sup>25</sup> This section summarises information on the German legal framework to provide a rough overview. However, a complete discourse on all the regulations is not intended in this study. The regulations may be found in corresponding laws, ordinances, or other documents.

In compliance with the federal structure of Germany, the implementation of environmental laws and decrees is under the responsibility of the federal states (Bundesländer), which may take into account local requirements and implement the administrative procedure differently. For new plants and also for major changes of existing plants a permission procedure with participation of the public has to be fulfilled. During the licensing procedure also an environmental impact assessment may be required (c.f. Gesetz über die Umweltverträglichkeitsprüfung (UVPG)).

Table 7-1 gives an overview of the German legal basis and regulations for environmental protection in Germany alongside the production line. In the following, a selection of most important acts, regulations and requirements is presented.

**Table 7-1: Legal basis and main regulations alongside the production line**

Area	Legal basis	Regulations and ordinances
Authorisation	Genehmigungsrecht	Bundes-Immissionsschutzverordnungen, ...
Transport	Verkehrsrecht	Gefahrgutverordnung Straße Gefahrgutverordnung Schiene Gefahrgutverordnung Binnenschifffahrt
Health and safety at work	Chemikaliengesetz (ChemG)	Chemikalienverbotsordnung Gefahrstoffverordnung
	Gewerbeordnung	TA Lärm Arbeitsschutzgesetz Arbeitsstättenverordnung und -richtlinien
Emissions	Bundes-Immissionsschutzgesetz (BImSchG)	Bundes-Immissionsschutzverordnungen Bundes-Immissionsschutzverwaltungsvorschriften (TA Luft, TA Lärm)
	Wasserhaushaltsgesetz (WHG)	- Abwasserverordnung (AbwV) - Indirekteinleiterverordnungen oder Abwassergesetze der Länder - Anlagenverordnungen der Länder - Katalog wassergefährdender Stoffe - Lagerung und Transport wassergefährdender Stoffe (VAWS)
Waste Prevention and Treatment	Kreislaufwirtschafts- und Abfallgesetz (KrW-/AbfG)	TA Abfall TA Siedlungsabfall
Environmental management		Öko-Audit ISO 14000

### 7.2.2.1 German regulations concerning the air quality

The basic law for air pollution control is the Federal Immission Control Act (Bundes-Immissionsschutzgesetz BImSchG). It primarily aims towards the protection of the medium air, but it also applies to the media water and soil in case pollution is transferred via the medium air. The BImSchG is specified by 21 ordinances and the Technical Instructions on Air Quality (TA Luft). Especially the TA Luft as a prescription for the authorities specifies in more detail requirements to be met by installations subject to licensing.

**Federal Immission Control Act (Bundes-Immissionsschutzgesetz, BImSchG)**

The BImSchG is the legal instrument for monitoring air pollution. Immission as defined within the law comprises air pollutants, and also noise, vibration, light, heat, radiation and associated factors affecting humans as well as animals, plants or other things. This concept already implements the idea of cross-media effects to a certain extent. The BImSchG requires federal authorities to issue ordinances identifying the types of facilities, which are subject to licensing, set licensing requirements for these facilities, and impose emission limit values and technical control requirements for all facilities, whether licensed or not.

Especially article 5(1)3 BImSchG aims at the avoidance and minimisation of wastes and residues. The paragraph emphasises the cross-media effects of industrial production. The concept of "state of the art technology" defined in the BImSchG is similar to the one of BAT:

*"State of the art as used herein shall mean the state of development of advanced processes of facilities or modes of operation which is deemed to indicate the practical suitability of a particular technique for restricting emission levels. When determining the state of the art, special consideration shall be given to comparable processes, facilities or modes of operation that have been successfully proven in practical operation."* (Article 3 paragraph 6 BImSchG)

In principle, "state of the art technology" is stated in terms of emission limits set by the licensing authority, the choice of technology to comply with the emission limit levels is left to industry. Necessary precautions against harmful effects on the environment are to be taken in particular by using control measures corresponding to the state of the art. Depending on the mass flow, some substances have to be measured continuously (e.g. SO<sub>x</sub>, NO<sub>x</sub>, and particulates).

**Technical Instructions on Air Quality (TA Luft):**

The Technical Instructions on Air Quality (TA Luft) [3] have been set up as general administrative regulations in connection with the §48 BImSchG (c.f. [18]). The TA Luft further specifies the requirements to be met by installations subject to licensing if not specified in one of the other regulations. Therefore, it prescribes limit values for virtually all air pollutants as well as structural and operational requirements designed to limit diffuse emissions. It establishes standards as well as assessment procedures for *immissions* (as suspended particles in [mg/Nm<sup>3</sup>] and as dust deposition [g/(m<sup>2</sup>d)]) and *emissions* [3]. Existing melting plants had to comply with the TA Luft (as at 1986) requirements by 1994. For the new federal states, the requirements had to be met before 1996, and in special cases by 1999. Table 7-2 shows the limits for main emission control requirements or, if specific regulations for non-ferrous metal production plants exist, it gives the corresponding more specific requirements laid down in the TA Luft, which are aimed at the avoidance and minimisation of air pollution.

The potentially emitted substances are split into different classes, whereby class I substances are the most toxic and while Class III are the least harmful. The emission limit values

contained in the TA Luft represent the BAT for technical measures for reducing emissions (dating from 1986). These quality values were developed referring to scientific findings and research taking into account toxicological, bioaccumulative and epidemiological aspects. The required concentration limits are given in mass of emitted substances related to the volume of emitted gas under standard conditions (0°C, 1,013 mbar) after subtraction of the water vapour content and for a prescribed measuring time and statistic evaluation (c.f. Section 4.1.8).

**Table 7-2: Emission control requirements laid down in the TA Luft**

Emitted substance (TA Luft section)	Class	Substances		Mass flow threshold [g/h]	Concentration limit [mg/Nm <sup>3</sup> ]
Dust containing waste gases (3.3.3.3.1 a))		dust containing waste gases are to be captured as far as possible and to be fed to a gas cleaning system, if necessary to comply with further requirements.			
Inorganic dust-like particles (3.1.4)	I	(e.g. Cd, Hg, Tl)	sum of substances	1	0.2
	II	(e.g. As, Co, Ni, Te, Se)	- " -	5	1
	III	(e.g. Sb, Pb, Cr, F, Cu, Mn, Pt, Pd, Rn, V, Sn)	- " -	25	5
	I+II		- " -		1
	I+III, II+III		- " -		5
Vaporous or gaseous inorganic substances (3.1.6)	I	(e.g. AsH <sub>3</sub> )	per substances	> 10	1
	II	(e.g. HF, Cl <sub>2</sub> , H <sub>2</sub> S)	- " -	> 50	5
	III	(e.g. Cl-compounds as HCl)	- " -	> 300	30
	IV	(e.g. SO <sub>2</sub> , NO + NO <sub>2</sub> as NO)	- " -	> 5,000	500
Organic substances (3.1.7)	I	(e.g. Chlormethane)	Classification	> 100	20
	II	(e.g. Chlorbenzene)	according to	> 2,000	100
	III	(e.g. Alkylalcohols)	Annex E of TA Luft	> 3,000	150
Carcinogens	I	(e.g. asbestos, benzo(a)pyren)		≥ 0.5	0.1
	II	(e.g. arsenic trioxide, dimethylsulfate)		≥ 5	1
	III	(e.g. Acrylonitrile, benzene)		≥ 25	5
Carbon monoxide (3.3.3.3.1)		should be utilised or burned as far as possible			

If inorganic dust particles of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/Nm<sup>3</sup> for coinciding class I and II substances as well as a total of 5 mg/Nm<sup>3</sup> for coinciding class I and III or class II and III substances.

If organic substances in several classes are present, the mass concentration in the emitted gas should not exceed a total of 0.15 g/Nm<sup>3</sup> with a total mass flow of 3 kg/h or more.

Furthermore, for facilities producing non-ferrous unrefined metals, particulate emissions in the emitted gases should not exceed 20 mg/Nm<sup>3</sup>. Sulphur dioxide and sulphur trioxide, indicated as sulphur dioxide, in the emitted gas of metallurgical plants should not exceed

0.80 g/Nm<sup>3</sup> at a mass flow of 5 kg/h or more.<sup>26</sup> When using solid or liquid fuels, a sulphur mass content of 1 %, which is given for solid fuels with a lower calorific value of 29.3 MJ/kg, should not be exceeded. For lead battery production plants, a limit value of 0.5 mg/Nm<sup>3</sup> for particulate emissions is given.

No daily mean value of the respective emitted substances should exceed the required emission limits, 97 % of all half-hourly mean values should not exceed 6/5 of the required emission limits, and no half-hourly mean value should exceed the required emission limits by more than twice.

Since the TA Luft stems from 1986, the local authorities demand stricter emission limit values.

#### **Ordinance on installations subject to licensing (4. BImSchV)**

In addition to these emission limits for certain substances shown in Table 7-2, special requirements for non-ferrous metal production plants are laid down in Section IV of the Bundes-Immissionsschutzgesetz (Verordnung über genehmigungsbedürftige Anlagen, 4. BImSchV) [12] for:

- roasting and sintering of non-ferrous metal ores,
- production of non-ferrous crude metals, and
- electrolytical production of zinc and lead.

#### **Technical Instruction on Noise Abatement (TA Lärm)**

The Technical Instruction on Noise Abatement (TA Lärm) [4] sets the limits for noise emission from the operation of a facility permitted in various areas. Permission for the construction, operation or altering of a facility is granted only if the emission limits allowed for a specific area are not exceeded and if state-of-the-art noise protection measures are employed.

In Germany, several organisations are working in the field of air pollution control on national level, for example the German *Länderausschuß für Immissionsschutz* (LAI) or the *Verein Deutscher Ingenieure* (VDI) and the *DIN Commission on Air Pollution Control*. Main topics of these organisations are to determine state of the art in process and environmental technology or requirements for the reduction of emissions. For example, the VDI/DIN Commission on Air Pollution is actually revising the technical guideline on the reduction of emissions from lead production plants [96]. In 1995, the LAI has published a concept concerning the restriction of PCDD/PCDF emissions from industrial production plants. For

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<sup>26</sup> Sulphuric acid plants are dealt with in a different section of the TA Luft. A conversion factor of at least 99.5 %/99.6 % for varying/constant gas conditions should be maintained. In addition, a sulphur trioxide limit value in the off-gas of 60 mg/Nm<sup>3</sup> for constant gas conditions resp. 120 mg/Nm<sup>3</sup> in all other cases should not be exceeded [3].

certain plants, the proposed concept recommends to consider, if a target value for PCDD/PCDF emissions of 0.1 ng-TE/Nm<sup>3</sup> can be realised. Thereby, plant-specific constraints (annual PCDD/PCDF emissions, technical options for the recycling of waste, costs for the installation of the emission reduction measures) have to be checked (c.f. [50]).

#### **7.2.2.2 German regulations concerning the water quality**

With respect to water management, each discharge, wherever it is located, has to comply with the Federal Water Act (Wasserhaushaltsgesetz, WHG [27]). The WHG is the legal instrument for water management, analogous to the BImSchG for air pollution control. It applies to waste water generated by various industrial processes, including the non-ferrous metal industry. According to the WHG, the use of surface, coastal, and ground waters requires the approval of the competent authority. Water protection legislation in Germany is implemented by the Ordinance on Waste Water (Abwasserverordnung, AbwV) Besides the minimum requirements concerning waste water treatment (c.f. Table 7-3), requirements concerning techniques of analysis and measurement as well as limits for the content of specific substances are laid down in the Annexes of the AbwV for different industries. The production of zinc and lead as part of the non-ferrous metal industry is dealt with in Annex 39 of this regulation [110]. In addition, the Federal Ministry of Environment has published explanations and comments on this Annex [13]. Depending on the local conditions, more stringent requirements can be established by the authorities.<sup>27</sup> Table 7-3 gives the main restrictions established in Annex 39 of the AbwV, especially for zinc and lead production plants.

The required load values shall be production-specific loads in relation to the production capacity on which the water discharge licence is based. It shall be determined by the 2 hours composite sample or the qualified random sample. The qualified random sample shall refer to a composite sample of at least five random samples taken over a maximum period of two hours at intervals of no less than two minutes, and blended. A composite sample shall refer to a sample which is taken continuously over a given period, or a sample consisting of several samples taken either continuously or continuously over a given period and blended. A random sample shall refer to a single sample taken from a waste water flow.

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<sup>27</sup> Each of the 16 Federal states has its own legislation which both the Federal Law and adds to it.

**Table 7-3: Limit values for discharges into water for non-ferrous metal production plants**

	<b>Limit value<sup>**)</sup></b> [mg/l]	<b>Load limit value<sup>***)</sup></b> [g/t tonne produced]
Cadmium	0.2	3 <sup>*)</sup>
Mercury	0.05	1 <sup>*)</sup>
Zinc	1	30 <sup>*)</sup>
Lead	0.5	15 <sup>*)</sup>
Copper	0.5	10 <sup>*)</sup>
Arsenic	0.1	2 <sup>*)</sup>
Nickel	0.5	15 <sup>*)</sup>
Thallium	1	-
Chromium, total	0.5	10 <sup>*)</sup>
Chromium VI <sup>****)</sup>	0.1	-
Cobalt	1	-
Silver	0.1	-
Tin	2	-
Cyanide (freely available) <sup>****)</sup>	0.1	-
Sulphide (dissolved)	1	-
AOX	1	-
Fish toxicity as thinning factor $G_f$	4	-
COD	-	1,500
Iron	-	100

<sup>\*)</sup> Only valid for plants with a daily production capacity of more than 10 tons.

<sup>\*\*)</sup> Qualified random sample or 2 hours composite sample; three from four samples have to comply with the limit and no value more than 100% exceeding the limit value

<sup>\*\*\*)</sup> The load limit is calculated with the permitted production capacity and the limit values given by permission

<sup>\*\*\*\*)</sup> This limit value is valid for the location where the waste water arises (c.f. [110]).

Source: Annex 39, Abwasserverordnung [13] bzw. [110]

Waste water from cooling systems for the indirect cooling of industrial processes is excluded from this regulation and subject to the provisions laid down in Annex 31, AbwV [13]. Table 7-4 gives the relevant requirements for discharges from cooling circuits in Annex 31 [110]. If the stated values are not observed, approval for the discharge of waste water will be denied.

**Table 7-4: Requirements for discharges from cooling systems of industrial processes**

Hazardous Substances	Minimal Requirements <sup>*)</sup>
COD	40 mg/l
Phosphor compounds, given as P	3 mg/l
Zinc	4 mg/l
AOX	0.15 mg/l
Available residual chlorine	0.3 mg/l
Chromium compounds	must not be contained
Mercury compounds	must not be contained
Nitrite	must not be contained
Metal organic Compounds (Metal-Carbon-Compound)	must not be contained

<sup>\*)</sup> Qualified random sample or 2 hours composite sample

Source: Annex 31, Abwasserverordnung [13] bzw. [110]

The WHG is furthermore complemented by the waste water levy act (Abwasserabgabengesetz: AbwAG) [25]. The tariffs are related to the mass and possible hazard of the discharged waste water according to Table 7-5. For the discharge of sewage, that exceeds the mentioned threshold values for concentrations or annual freights, the discharging party has to pay a levy related to the given units of measurement.<sup>28</sup>

**Table 7-5: Thresholds according to the waste water levy act**

Hazardous Substances	Units of measurement (relating to a unit of hazard)	Threshold values	
		Concentrations	Annual freights
COD	50 kg Oxygen	20 mg/l	250 kg
P, total	3 kg	0.1 mg/l	15 kg
N <sub>2</sub> , total	25 kg	5 mg/l	125 kg
AOX	2 kg Halogen, calculated as Cl	100 µg/l	10 kg
Hg	20 g	1 µg/l	0.1 kg
Cd	100 g	5 µg/l	0.5 kg
Cr	500 g	50 µg/l	2.5 kg
Ni	500 g	50 µg/l	2.5 kg
Pb	500 g	50 µg/l	2.5 kg
Cu	1000 g	100 µg/l	5 kg
Fish toxicity (G <sub>f</sub> )	3,000 m <sup>3</sup> discharges divided by G <sub>f</sub>	G <sub>f</sub> = 2 (dilution factor for non-lethal quantity for fish from the discharge)	

Source: Abwasserabgabengesetz [25]

<sup>28</sup> At the moment, a levy of 70 DM per unit of hazard has to be paid.



### 7.2.2.3 German regulations concerning the waste management and disposal of hazardous materials

Waste legislation in Germany is laid down in the Act on Waste Prevention and Treatment (*Gesetz zur Vermeidung, Verwertung und Beseitigung von Abfällen, GVVB* [28]). It is applied to the use and storage of waste, i.e. to substances to be disposed of by the processor or to substances whose proper treatment is necessary to protect the environment. Additional requirements refer to waste from particular installations.

Legislation laying down measures aiming towards "avoidance, utilisation and disposal" of waste is set down in the Federal Recycling and Waste Management Act (*Kreislaufwirtschafts- und Abfallgesetz, KrW-/AbfG* [26]), which came into force in October 1996 and is the most important part of the new GVVB. It broadens the entire national waste concept and sets new priorities with regard to the avoidance of and the duty to utilise waste. The KrW-/AbfG also codifies manufacturer's product responsibility.

For administrative procedures, technical guidelines on waste (TA Abfall, [1]) and on municipal waste (TA Siedlungsabfall, [2]) are of relevance. The TA Abfall regulates planning, licensing, construction and operation of waste disposal facilities [78]. Facilities for treating waste have to fulfil requirements regulated in special decrees, based on Art. 5 BImSchG.

A working group of the federal states on waste (*Länderarbeitsgemeinschaft Abfall, LAGA*) issued a categorisation of waste types, comprising 589 types of waste, of which 333 have priority for control (*LAGA-Abfallartenkatalog*, [52]). This catalogue was valid till 12/31/1998 and has been replaced by the European waste catalogue (EWC) in the following [55]. To facilitate the change from the LAGA catalogue to the EWC, the German LAGA worked out an interim catalogue (*LAGA-Umsteigekatalog*, [51]). According to this categorisation, the following types of waste may arise within the zinc and lead production industry (c.f. [52, 51]):

- slags from non-ferrous metal melting,
- plant residues (runner breaks, ladle breaks, converter breaks, refractory breaks, etc.),
- sludges from non-ferrous metallurgy, and
- filter dust.

### 7.2.3 International regulations (overview)<sup>29</sup>

In this section, a rough overview of important regulations on an international level effecting the non-ferrous metal production industry is given. International regulations and agreements have been worked out on different levels. Besides the European level, which is not further considered in this chapter, the different international committees of the United Nations like UNEP, UNCED, UNECE, WHO, IFCS have to be mentioned. In addition, the OECD is working in the field of environmental protection. Important international regulations, effecting the pollution of the different environmental media are e.g.:

#### **Long Range Treaty on Air Pollution (UN/ECE)**

International efforts to reduce the adverse effects of the transboundary acidification on forests, aquatic ecosystems, and human health, by way of internationally co-ordinated emission reductions, were undertaken in the 1979 *Convention on Long Range Transboundary Air Pollution* (LRTAP). After coming into force in 1983, the LRTAP Convention was augmented by (1) the 1984 Protocol on long-term financing; (2) the 1985 Helsinki Protocol reducing sulphur emissions or their transboundary fluxes by at least 30%; (3) the 1988 Sofia Protocol on the freezing of the emission of nitrogen oxides; (4) the 1991 Geneva Protocol on the control of the emission of volatile organic compounds; and (5) the 1994 Oslo Protocol on the further reduction of the emission of sulphur dioxide.

#### **Basel Conventions (United Nations)**

The Basel Conventions declare the responsibility of OECD states regarding the control of transboundary movements of hazardous wastes and their disposal. It was adopted in March 1989 and entered into force in May 1992. In 1996, more than 100 countries plus the EC are parties to the Convention. The conventions comprise Technical Guidelines for waste management activities. In this guidelines materials are divided into substances with a ban for export (list A) and substances which still can be exported to non-OECD countries. A decision adopted by the parties in 1994 prohibits with immediate effect the export from OECD countries of hazardous wastes destined for final disposal in non-OECD countries. The decision also phased out similar exports destined for recycling or recovery operations before banning them completely on 31 December 1997.

#### **OECD-Council decision on Transfrontier Movements of Hazardous Wastes**

As a reaction of the "Basel Convention" of the United Nations, the council of the OECD ratified the council decision C 88(90). A three-tiered system was proposed to delineate controls to be applied to transfrontier movements: Wastes destined for recovery operations

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<sup>29</sup> This section summarises information on international regulations effecting the non-ferrous metal industry. However, a complete discourse on all the regulations is not intended in this study. The regulations may be found in corresponding laws, ordinances, or other documents. A more detailed summary can be found in [46]

included on the green list would move among OECD Member countries toward recovery operations subject to all existing controls normally applied in commercial transactions. A notification procedure would exist for wastes destined for recovery operations included in the yellow list and wastes destined for recovery operations included in the amber list or red list would be subject to stricter or more rigorous controls.

### **Protection of the aquatic environment**

There are several international activities concerning the protection of the aquatic environment. The most important ones are the Oslo Paris Commission (Osparcom) for the protection of the maritime environment of the North Sea and the Northeast Atlantic and the Helsinki commission of the countries bordering the East Sea (HELCOM) for the protection of their maritime environment.

In addition, there exist several international agreements on the pollution prevention of the main European seas (Nordseeschutzkonferenz), lakes (Bodensee) and rivers (e.g. Rhine (IKSR), Elbe (IKSE), Donau (IKSD), Oder (IKSO)) [46]. For example, there are two international agreements dating from 1978 concerning the pollution prevention of the River Rhine referring to chemical contamination and chlorides [85].

### **Global Environment Monitoring System (WHO/UNEP)**

UNEP and WHO operate the GEMS (Global Environment Monitoring System) environmental pollution monitoring programmes for urban air quality (AIR), food, human exposure assessment location (HEAL), and water. The objectives of GEMS as defined at its inception are:

- to strengthen monitoring and assessment capabilities in the participating countries,
- to increase the validity and comparability of environmental data and information,
- to produce global/regional assessments in selected fields and compile environmental information at a global level.

